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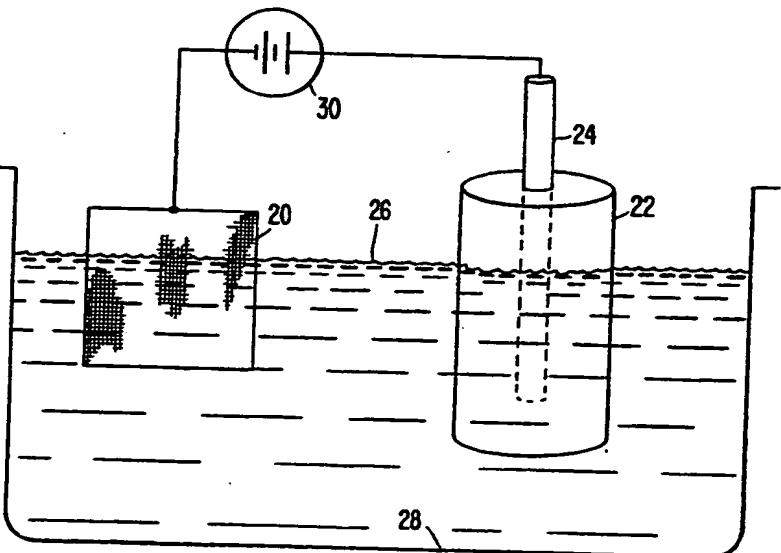
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(54) Title: METHOD OF REMOVING IONS

(57) Abstract

Remediation of soil and groundwater-bearing aquifers by the use of an ion immobilizing matrix introduced into a bulk liquid or soil either as a membrane covering or as a canister or similar suitable configuration. The ion immobilizing or host receptor matrix is associated with, and may envelop, at least one electrode. An oppositely charged electrode is located at a distance from the enveloped electrode, with the contaminated bulk therebetween. An electropotential is established which causes the ionic species to migrate through the water or soil and ultimately to become immobilized in the host receptor matrix. Once the host receptor matrix is fully loaded, it can be withdrawn and disposed of as a solid waste form. In one configuration, the electrode is imbedded within the host receptor matrix. In another configuration, the electrode is positioned inside an ion reservoir confinement chamber which has as one surface an ion permeable membrane optionally in contact with an immobilizing ion exchange polymer. The host receptor matrix can be an ion-conductive organic polymer membrane composite which may incorporate ion exchange media or selective absorbent materials as fillers, or optionally a medium that can facilitate both ion transmission and complexation which can insolubilize the mobile ionic media thereby yielding a stable repository for the ions being captured. This apparatus and method provides a solid wasteform which can be easily and safely removed for disposal and which is practical for volume reduction by incineration. Alternatively, a host receptor matrix is provided which permits rapid discharge of ions from the matrix when the electropotential is reversed.



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Description

"Method of Removing Ions"

This application is a continuation-in-part of application Serial No. 07/348,525, filed July 21, 1989.

Technical Field

Background Art

Disclosure of the Invention

The present invention relates to a process and apparatus for removing ionic materials such as radionuclides or heavy metals from soils and aqueous media by electropotential ion transport and an ion immobilizing matrix.

The contamination of soil, aquifers and vegetation by ionic materials such as radionuclides and/or heavy metals increases the potential entry of such toxic materials into human organisms via biological and food chains. Scientific study of this phenomenon has been ongoing for decades. Ultimately, the objective of such study is to identify methods for decontamination in order to decrease the amount of undesirable ionic materials carried by the soils and aquifers.

Ions of heavy metals, radioactive cations, and certain undesirable anions can be toxic to humans. In many instances, they can be retained in the human body and accumulated over a long term to such an extent that exposure to extremely low concentrations can present health concerns. Human health concerns dictate a diligent effort to remediate such contamination.

A most direct method for removing ionic contaminants from groundwater and soils is by excavating the contaminated subsurface materials, such as soils, sediments, fractured rock, and by processing same in a manner that will incarcerate the ions. An alternative technique has been proposed which provides an impervious covering over the ion contaminated regions, which essentially immobilizes the ion by preventing the intrusion of groundwater, an essential electrolyte which enables ion mobility. More recently, an effort has been pursued which involves in-place vitrification of the entire soil strata, wherein a "frit" is added to the soil and an intense electrical field is established which turns the soil into a glass-like mass whereby leech of the ion is stymied.

Other methods for isolating contaminants have been proposed. For example, U.S. Patent No. 3,723,338 provides for injecting a polymerizable monomer, and U.S. Patent No. 4,156,658 discloses injecting an ion exchange gel. These methods suffer from significant shortcomings because the agricultural usefulness of the soil is destroyed. The processes thus do not satisfactorily alleviate the problem, and also are expensive.

Still another process involves soil washing, wherein surfactant chemicals and/or pH adjustments are used to remove soil contaminants and thereby enable the cleansed soil to be returned to service. Disadvantages are that very large volumes of radioactive waste are produced and the process is very expensive.

Still another prior practice has been to excavate contaminated soil for transport and burial at a remote site away from human inhabitants. Another prior process involves radionuclide contaminant reduction via removal of surface vegetation and/or the surface layers of top soil. The principal drawback of these techniques is that the problem is simply relocated, i.e., large quantities of contaminated soil

and waste are simply transported from one location to another and very little actual decontamination of the soil takes place.

Another approach which has been studied would simply mitigate the problem by burying the contamination by deep plowing using special machinery. This method would, in theory, place the radioactive materials deep enough to prevent contact with the roots of crops. This method is expensive and, more importantly, is not an environmentally acceptable approach.

Still another approach is to change the land usage, either by removing the land totally from agricultural use or by planting crops such as sugar or oil crops (soybeans) or possibly forestry, whose nutrition does not involve uptake of radionuclides or whose end use does not place such radionuclides in the food chain. Further, this approach fails to address problems of wind blown dusts, ground water contamination and related toxic contamination phenomena.

Various thermal processes have also been proposed which either result in removal of radiocontaminants via a vapor release, or in some instances, through calcination or incineration. However, these too are expensive, complex and destructive to the soil.

The above methods are regarded as, at best, only marginally effective in achieving their goal, namely permitting the return of contaminated land to its original use.

In the case of contamination of underground aquifers, much of the technical assessment has concluded that remediation is so impractical that the only economical means for mitigation involves an identification and isolation of the source of contamination and a prolonged delay in human contact until natural diffusion of water through the aquifer can provide for dilution of the contaminant.

In some instances, groundwater in the aquifer can be removed via a pumping system, processed through conventional

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ion exchange media and subsequently, reinjected into the ground.

Another, more popular alternative, provides for a similar cleanup of the subterranean groundwater at the point of its use. Such technology has found widespread use in municipal water treatment facilities where well water can be processed through ion-exchange beds and/or charcoal absorber beds. However, such an approach does not represent an actual in-situ cleanup. The result is that the aquifer remains contaminated and a private well tapping such an aquifer would use a contaminated water source.

Still another option involves in-situ treatment wherein chemicals are introduced which react with the ionic contaminants to form insoluble precipitates. This process has not met with general acceptance due to potential for a difficult-to-control chemical interaction between subterranean water and surrounding mineralogy.

Another drawback of current methods for groundwater cleanup is that cleanup is so expensive that users are compelled to accept less than "clean" water.

In the past, cesium contaminated soils have posed a major obstacle to soil cleanup programs. The difficulty relates to the low mobility of heavy metals such as cesium and plutonium in soil. This low mobility presents two counterpoised factors.

First, these are long-lived radioisotopes which time and natural weathering will not remove, thus some kind of active intervention by man is essential for their decontamination.

Second, the deposited contaminants are not prone to move rapidly and/or reach ground water sources, and thus the situation has not been viewed as critical.

The above described factors have contributed to the buildup of a substantial inventory of contaminated sites across the country.

It has been shown that clays provide the repository for deposited cesium. For example, Gale et al. in 1964 showed

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that 70% of the total cesium was within the 13% clay fraction of a sandy loam. Lomenick and Tamira in 1965 made measurements of lake sediments and concluded that 84% of the cesium was associated with the 35% clay fraction. Also it has been found that interleaved mica, which is a constituent of this sediment, was the receptor for the cesium.

In the past, it has been concluded that the association of cesium (and its relatives in the heavy metal family) is essentially irreversible. Thus, it is frequently stated that the cesium is "fixed" by the clay.

An example of this consensus is contained in a literature review on this subject made by Howorth and Sandalls in 1987 under sponsorship of the United Kingdom Atomic Energy Authority, titled "Decontamination and Reclamation of Agricultural Land Following a Nuclear Accident", wherein on page 7 of the article the statement is made "... methods which aim to leach cesium from the soil are unlikely to be successful".

The significance of the above conclusion becomes apparent when considering that the cage structure of muscovite mica, which is a component of soil clays, is very similar to that of the zeolite, chabazite. Soil clays are present in a percentage ranging from 10-25 percent in virtually every fertile soil in the world.

Heretofore the prospect for removing such heavy radioactive species from the soils has been so difficult as to be considered impracticable. The reasons for this difficulty lie in the atomic characteristics of these heavy metals, especially in their ionic state ("M⁺"). Generally, the larger the M⁺ ion, the more numerous are its insoluble salts. One of the important properties of heavy metal ions is their tendency to become bound in a zeolite in insoluble form.

This phenomenon involves a cage-like ion trap found in zeolites, which is responsible for the zeolites often being referred to as an ion sponge or ion exchanger. An example is the cesium ion (Cs⁺) which is routinely encountered in

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radioactive form when dealing with fission-type nuclear power or nuclear weapons. The crystal radius of this cesium ion is 3.4 angstroms and the hydrated radius is 6.6 angstroms. The zeolite mineral of the chabazite class has receptor sites whose pore size ranges from 3-7 angstroms which is such that the cesium will fit nearly perfectly into this "host-cage-structure". By comparison, a smaller ion (sodium for example) would tend to be more weakly bound in the cage, and upon the arrival of a cesium ion, would be easily displaced.

One prior art approach to plutonium decontamination from soil involved development of a mobile decontamination unit at the Rocky Flats Plant, U.S.A. which was designed to treat 9,000 kilograms of soil per hour. The result was that the unit separated the clay from the non-clay fraction and the contaminated clay was transported to a licensed site for burial. The conclusion of this effort was that the volume of radioactive waste was still too high, the cost was too great, and the capacity even at 9,000 kilograms per hour was too small to be viable.

Another mitigation method which has been studied is soil "stabilization" work done by James and Menzel in Beltsville, Maryland, 1960-1961. This involved use of asphalt - road oil-paint and such to seal the soil, and is reported to be virtually ineffective.

Another method studied in the past has been removal of ions through crop uptake. The work to date concludes that the uptake is sufficiently low to be of limited practical significance.

Another method involves the addition of fertilizers. For example, use of potassium-based fertilizer was attempted on the Bikini Atoll. The result was measured in the uptake by coconut meat and milk, where a 90% reduction in uptake of cesium was observed. The conclusion was that if the potassium levels get low, the plants adjust by taking up the cesium. Therefore by keeping potassium high, the problem can be mitigated. (See R.M. Aleksakhin, Akade Miya Nauk, SSSR, "Radioactive Contamination of Soil and Plants", Moscow,

1963). On the other hand, nitrogen fertilizers had a reverse effect, actually increasing the cesium uptake by the plants. This work with fertilizers did not consider the fertilizer as providing a means for decontaminating (by radionuclide removal) the soil, but rather as a means for altering the plant's uptake of the radionuclides resident in the soil.

Many of the currently employed methods for decontamination of water and soils involve some form of diffusion-controlled ion exchange.

One of the world's largest plants for treatment of effluent from a spent nuclear fuel plant is the British Nuclear Fuels, Inc., SIXEP Plant. The SIXEP process is based on ion exchange using an inorganic ion exchanger. In this process, the positively charged cesium and strontium ions are taken up into the crystal lattice of clinoptilolite (a class of porous crystalline aluminosilicates of the zeolite family), in preference to the sodium ions which are naturally present. In this process, water containing the radioactive ions is caused to pass into close proximity to the clinoptilolite, whereupon diffusion takes place to cause migration of the ions into the clinoptilolite lattice, wherein the sodium ions are displaced by the cesium and/or strontium ions.

In extracting ionic species from groundwater, including the runoff from ion-contaminated soils, the practice called "pump-and-treat" can be utilized. This method suffers from numerous problems and economic disadvantages. The method encompasses collecting the water and pumping it through a suitable aqueduct to ultimately bring the water bearing the contaminant ions into close contact with an opposite charge-carrying ion exchange receptor material. Therefore, large containers of the ion exchange receptor material, so called ion exchange beads, must be used. The media can be either organic or inorganic. Either category is available in anion exchangers or cation exchangers and in many cases, specific applications will call for blends of both.

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An example of organic polymer materials functioning as cation exchangers are the styrene di-vinyl benzene matrix polymers incorporating sulfonate end groups. Anion exchangers (for example, GT-73 by Rohm & Haas) typically include a quaternary ammonium site normally coupled with an amine moiety.

In the prior art, contaminated water would typically be pumped from its repository into a vessel confining an ion exchange resin bed, the vessel consisting of a shell whose volume provides the necessary residence time, an adequate throughput and sufficiently long bed life.

There are many ion exchange compositions that satisfy the desired characteristics and function well in a diffusion uptake regimen. For example, early sulfonic resins based on a cross-linked phenolic matrix have been utilized as diffusion-type ion exchange compositions. These resins can be prepared either by sulfonation of phenol-formaldehyde polymers (Amberlite IR-100), by condensation of phenolsulfonic acid with formaldehyde (Dowex 30), or by alkaline condensation of sodium phenoxide, sodium sulfite, and formaldehyde (Amberlite IR-1).

Another class of diffusion-type ion exchange media is the strong-acid resins which are typically sulfonated styrene-divinylbenzene copolymer products (Amberlite IR-120, Amberlite IR-200, Dowex 50, Dowex 50W, Dowex MPC-1, Duolite C-20, Duolite C-25, Ionac C-240, and Ionac C-250). All are spherical products prepared by sulfonation of styrene-divinylbenzene copolymer beads with a sulfonating agent.

Another class of ion exchange media, the weak acid resins, are typified by the presence of functional groups consisting of phenolic, phosphorous, $RP(OH)_2$, or carboxylic entities. They can be prepared by cross-linking an unsaturated carboxylic acid such as acrylic, methacrylic or maleic with a cross-linking agent such as divinylbenzene or ethylene dimethacrylate. A large number of these structures have been prepared in the laboratory using various tertiary

amines. Popular commercial materials are Amberlite IRA-400 series, Duolite A-101 series, Dowex and Ionac A-540.

Another category of diffusion-type ion exchanger is the strong base anion-exchange resins. These are prepared from the reaction of chloromethylated beads with a dialkyl sulfide such as dimethyl sulfide to produce a disulfonium compound. This is contrasted with the weak base anion-exchange resins which contain primary, secondary, and/or tertiary amine groups, generally a mixture of these. A wide variety of products are available, generally condensation products of aliphatic polyamines with formaldehyde or with alkyl dihalides, such as ethylene dichloride, or with epichlorohydrin.

"Snake-cage" polyelectrolytes are known and have been developed for specific purposes; they consist of a cross-linked polymer system ("cage"), containing a physically trapped linear polymer ("snake"). These are physically constrained mixtures of polymers. The cage polymer restricts the freedom of kinetic motion of the snake polymer. An example is: Retardion 11A8 (The Dow Chemical Co.).

Certain of these structures are useful for specific ions. A good example of this is the unusual affinity for cesium exhibited by dipotassium cobalt(II) hexacyanoferrate(II), $K_2CoFe(CN)_6$, precipitated in the form of reasonably sized granules. (R. Harjula et al., University of Helsinki, Union Inkatu, 35, Helsinki, Finland, "Removal of Cesium from Nuclear Waste Solutions...", 1985). In more recent work, attention has been focused on optimizing ion transport through polymeric media. The structure and porosity of an ion exchange resin are determined principally by the conditions of polymerization of the base ("backbone") polymer, to which the ionic sites are pendant as mentioned above, to polyelectrolyte materials which are immobilized within a matrix.

Mass polymers prepared in the presence of major amounts of nonpolymerizable diluents were reported by U.S. Patent No. 2,800,445 to Clarke, who showed their utility in the

preparation of ion exchange membranes. Macroporous ion exchange resins (sometimes referred to as "macroreticular" or "isoporous") have been prominent since about 1960. For example, in U.S. Patent No. 3,808,305, Gregor discloses an interpolymer membrane of a matrix polymer, a polyelectrolyte and a cross-linker to achieve desired pore size. Such resins have pores of a considerably larger size than those of the more conventional gel-type resin. Pore diameters of up to several thousand angstroms are typical. Although these were available in bead form, the major focus was placed on a membrane geometry. Because the pores could be varied tremendously in both size and uniformity, the membranes could be precisely designed for desired selectivity.

Ion exchange membranes produced from these macroporous polymers exhibit distinguishable properties, namely they are capable of providing one-way conduits for certain size ions while restricting passage of large species.

In the prior art, a typical process for manufacturing such a membrane involves casting the membrane from a solvent/polymer blend solution comprising approximately 20% solids solution in a polymer such as butyralactone (see U.S. Patent No. 2,957,206), force-curing to insure complete solvent evaporation, then treating the membrane with a polar liquid (i.e., water). Typical matrix polymers have heretofore been vinyl halides, styrene or acrylic. The polyelectrolyte can be polystyrene sulfonic acid or poly acrylic acid (Mol. wt. 4000) or onium class (Quaternary Ammonium Groups). Generally, these films run 3-6 mils thick. Multiple layering is required for up to 25 mil thick films.

In more recent technology, novel electrochemical cells incorporating these ion exchange membranes have been used to rid water of metal ion contaminants in an economical manner. Many variations have been proposed to enhance operation of ion membranes for this service. For example, U.S. Patent No. 3,227,662 addresses depolarization of the membrane surface in brackish water cleanup.

Electrochemical cells have generally not been favored for work involving radioactive contaminant metals, because the waste form (or concentrated effluent) is liquid. Scientists working with radiochemicals generally prefer solid material whenever possible, which solid material is realized with the prior art bead-type of ion exchanger.

Electrochemists have continually sought to devise practical ways to adapt this ionic electrical mobility phenomenon for use in dealing with radionuclide and heavy metal-bearing contamination.

Ion exchange membranes are particularly suited to electrochemical processes in which the object is to produce pure chemicals. Ions in solution (either cations or anions) can be caused to migrate through a membrane by application of a voltage. The electrical power involved is frequently more economical than use of chemical agents.

There are some widely recognized, basic cell designs that have heretofore been used in electrodialytic demineralization of water. An example is found in U.S. Patent No. 2,636,851 to Juda, which describes an electrodialysis process using a single membrane to purify water.

In further refinement of the technology, U.S. Patent No. 4,632,745 to Giuffrida, describes a two-compartment cell, which consists of a multiplicity of anode and cathode compartments separated by either an anion permeable or cation permeable membrane; water containing various salts is the electrolyte. Under an impressed potential, positive ions migrate readily through the cation permeable membrane out of the anode chamber into the cathode chamber, and at the anode, hydrogen ions are produced and oxygen is liberated. Migration of hydroxyl ions toward the anode is substantially impeded by the permselective cation exchange membrane.

There are numerous literature references involving the use of a single ion exchange membrane separating two electrode chambers, as well as multiple compartment cells. These processes all involve liquid solutions with substantial

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operational complexities. Specifically, liquid radioactive solutions are utilized that are difficult to confine and immobilize into solid wasteforms.

An example of another electrochemical cell of still further operational complexity is the three compartment cell which uses two membranes. A solution can be depleted of its salinity by electrolysis in a three-compartment cell employing both a cation and an anion permeable membrane. (See U.S. Patent No. 3,869,376). In this cell, one of the compartments, namely the center compartment, is filled with ion exchange material. An electropotential is applied between electrodes which drives cations into the cathode chamber to form alkali and drives anions into the anode chamber to form acids. Use of three compartments is to protect an electrode from a particular electrolyte or an electrolyte from an electrode reaction or, in the case of the electrodialysis of water, to provide a medium for concentration of the aqueous waste streams.

The literature disclosures numerous variations on the electrodialysis cells employing multiple membranes between the electrodes. In particular, an arrangement of alternating anion permeable and cation permeable membranes between an anode and cathode has been used for deionizing electrolyte solutions with a minimum expenditure of power. This type of cell is called the multiple ion exchange membrane electrodialysis (MIEME) cell. (U.S. Patent Nos. 4,632,745, 3,149,061, and 2,815,320).

Those skilled in the art of water purification are aware that removing soluble salts from water has been a major focus of electrodialysis. Recent advances in synthetic ion exchange membranes have greatly stimulated interest in the dionization of saline and brackish waters by electrodialysis. (See U.S. Patent No. 3,808,305).

For example, devices consisting of an indefinite number of chambers alternately separated by positive and negative membranes have been disclosed. By imposing a D.C. current, it is possible to deplete the solution in alternate chambers

while concentrating that in the others. A unit cell consists of a depletion chamber and a concentration chamber. The electrode chambers are supplied independently to keep the electrode reaction products separate as well as to separate the concentrated or depleted electrolyte streams. Where sodium chloride is the electrolyte, chlorine and oxygen will be evolved. The contents of the anode chamber will become acidic and hydrogen will be evolved at the cathode, along with the formation of sodium hydroxide.

It is possible in principle to predict the flow characteristics, power requirements, and efficiencies of any electrodialysis cell if the electrochemical properties of the membranes and solutions, as well as the mechanical transport properties of the solutions through the membranes, are known under a wide range of conditions.

The main disadvantage of the existing electrodialysis technology rests in the fact that it cannot be used in an in-situ remediation or cleanup of either soil or groundwater.

Also, these prior art cells suffer from the disadvantages of relatively complex operation, the requirement for substantial capital investment in operating hardware, and the fact that they generate a liquid waste form, and in the case of U.S. Patent No. 3,808,305, a very large volume of waste. Most importantly, none of these are able to remove soluble ions from a bulk medium.

In the prior art technology, the mechanism of ion diffusion has heretofore controlled the speed with which ion exchange takes place. Also, this has heretofore determined the portion of the equilibrium capacity which may be utilized in a practical dynamic situation. In deionization column operations, the actual operating rates have been found by operating experience to be less than the theoretical diffusion rates.

Efforts at optimization of exchange rates have focused on utilizing ion exchange resins which are highly swollen. Additionally, exchange rates are more rapid in lower cross-linked resins of the same dry-basis capacity because of the

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higher moisture uptake. The ion exchange process involves diffusion through the film of solution in close contact with the resins, and also diffusion within the particle of resin itself. Film diffusion becomes rate-controlled at low concentrations, particle diffusion controls the rate at high concentrations. The particle size of the resin is also a determining factor.

The above phenomenon presents one significant departure between the prior art and the present invention. The present invention provides a receptor polymer matrix whose unique composition enables both ion transport and subsequent immobilization in a single composite envelope and also provides a decontamination apparatus which can function in a virtually passive means as an in-situ soil and groundwater cleanup system, and which can function without compromising the agricultural potential of the soil.

It is an object of this invention to provide an improved method for decontaminating a bulk media such as soil or groundwater.

Another object of this invention is to provide an improved method for fixing and for transporting undesirable contaminant ions.

A further object of this invention is to provide a practical means for groundwater and soil remediation to be carried out in-situ.

Another object is to provide a method whereby radionuclide contaminated groundwater can be treated in place without the need to pump the water to the surface.

Another object of the invention is to effectively decontaminate soil of ionic contaminants, with a minimum of excavation, transport, and handling.

Another object of this invention is to provide a concentrator/collector medium which is in solid form, thereby eliminating the need for secondary processing steps to achieve a concentrated, solidified and transportable form.

Another object of this invention is to provide a processing system requiring a minimum of human intervention,

namely a process that will operate reliably over the long term without significant adjustments or maintenance.

Another object of this invention is to remove unwanted ions from soil while leaving the soil at least as useful agriculturally as it was prior to the process, and more preferably in an enriched state.

Another object of this invention is to provide a means for effectively remediating ground water and/or soil contaminants with a minimum of exposure to operating personnel.

Another object of this invention is to provide a mechanism for intercepting ion contaminants via a solid wasteform, which wasteform can be processed under controlled conditions. Another object of this invention is to provide a means for decontaminating an aqueous stream, a slurry, or a soil medium where the contaminated medium is transported to a suitable vessel, and the process is carried out within such vessel.

Another object of this invention is to extract contaminants which are non-ionic, but which can be caused to behave as ionic species via the introduction of ionic surfactants or charged polymeric media.

The present invention, as embodied and broadly described herein, overcomes the problems and disadvantages of the prior art and achieves the aforementioned objects in accordance with the purpose of the invention by providing a process for extracting ions from a bulk source. The process comprises introducing a host receptor matrix into contact with the bulk source. Ions are then induced to migrate from the bulk source into the host receptor matrix by means of an external electropotential gradient. The matrix is then removed from the bulk source. The matrix provides a means for immobilizing the ions and facilitates the maintenance of a substantial electropotential over the desired ion removal period.

The present invention also provides an apparatus for extracting ions from a bulk source. The apparatus comprises

a pair of electrodes, means for creating an electropotential between the electrodes and an ion conducting polymeric host receptor matrix which is associated with at least one electrode. The matrix is receptive to the ions to be extracted and the matrix and the electrodes are configured to facilitate maintenance of a substantial electropotential over the desired ion removal period.

The invention further provides a host receptor matrix useful for electrochemically removing ionic materials from a bulk medium. The host receptor matrix comprises a mass polymer which provides structural integrity and an ion conductive polymer having pendant ion exchange sites.

The invention also provides an in-situ extraction process useful for removing ions from a bulk source. The process comprises inducing ion migration through at least one ion permeable membrane by means of an external electropotential. The ions are then collected in a confinement chamber, and may subsequently be disposed of by transporting them to an appropriate processing or burial site.

The invention further provides a process for removing ionic solutes from a bulk source. The process comprises imposing an electropotential by means of a pair of electrodes, at least one of which is substantially enveloped by a hydrophilic host receptor matrix. The process also includes collecting the ionic solutes which are transported by the electropotential to the host matrix. The process may also include removing the matrix from the bulk source and subsequently reversing the charge on the electrodes to force the ionic species out of the matrix.

The invention further provides an apparatus for extraction of ionic species from a bulk source. The apparatus includes two oppositely charged electrodes, at least one of which includes a structurally stable host receptor matrix. The apparatus has a configuration that can accommodate introduction and retrieval of the host receptor matrix from a region proximate to the bulk source. The host

receptor matrix is capable of receiving and retaining the ionic species.

Brief Description of the Drawings

Figure 1 is a schematic drawing of electrical extraction of cations from soil using a host receptor matrix in spray applied or sheet membrane form.

Figure 2 is a schematic drawing showing an electrode array for in-situ electro-extraction using a host receptor matrix.

Figure 3 is a diagram of a laboratory scale electropotential/polymer immobilization cell used to model a cleanup of an underground aquifer.

Figure 4 is a diagram of an electro-extraction cell for remediating contaminated groundwater.

Figure 5 is a diagram of a laboratory scale apparatus used to conduct electro-extraction heavy metal-containing soil samples.

Figure 6 is a diagram of a laboratory scale apparatus used for in-situ groundwater remediation.

Figure 7 is a diagram of an electro-extraction cell utilizing a ceramic foam host receptor matrix.

Best Mode for Carrying Out the Invention

The present invention provides a method of treating water dampened soils or groundwater streams that have been contaminated with radioactive materials and/or metal cations and/or anionic materials. This process involves causing ions to migrate under an externally applied electropotential to a receptor material wherein they ultimately become immobilized. The method utilizes a host receptor matrix which surrounds the electrode. It is believed that the immobilization is accomplished in part due to the phenomenon of ion exchange; optionally, in part by ion concentration within interstitial water domains which are a part of the host receptor matrix; optionally, in part by precipitation which occurs within the host receptor matrix; and optionally, in part by electrolytic reduction at the cathode.

In accordance with the invention, ionic species in a bulk source can be mobilized by an electrical potential which causes the target ions to migrate across the ion bearing bulk source which separates a pair of electrodes. As cations approach the cathode, they encounter a special polymeric matrix which acts as the host receptor matrix. The matrix functions to provide ion transport until these positively charged species encounter and are immobilized by one or more of the following: by cation receptor sites grafted onto the polymer chain; when an ion exchange filler is encountered, such as a zeolite; when a zone of very high pH is encountered; or when the ion is reduced to metal at the cathode. Just as the cation mobilization and immobilization takes place, anion species can be correspondingly collected in a polymeric host receptor matrix at the anode.

In one embodiment of the invention, the host receptor matrix is in the form of a membrane which can be spread over a soil surface. By inducing ion migration by application of an electropotential, a means is provided for removing radioactive contaminants or other ionic contaminants from soils. The host receptor matrix membrane simultaneously accommodates both ion transport and ion immobilization. In certain soil contamination scenarios, such a membrane can provide a very efficient and effective geometry for ion transport between the two electrodes due to the large surface area that is in contact with the contaminated zone. In this embodiment, the host receptor matrix is preferably a highly elastomeric composite such as a polyurethane/polyol copolymer or an acrylate/methacrylic acid copolymer.

Another embodiment of the invention provides for liquid ion exchangers and/or fine particle size ion exchange materials and a polymeric host receptor matrix which can be mixed with polymerization coreactants and applied in liquid form such that the solution can conform to surface contours. The host receptor matrix polymer subsequently cures to a highly elastomeric sheet, retaining its ion transport properties, which enhances the handling characteristics

during removal. An illustrative use for such a liquid applied, curing type membrane material could include application of this membrane host receptor matrix to the internal surfaces of a metallic storage tank or mixing vessel prior to filling the tank with a contaminated medium. In such case, the polymer membrane would have only a minimal adhesive bond to the vessel shell. Upon completion of the electropotential induced ion uptake cycle, the polymer membrane, loaded with contaminant ions removed from the bulk, is readily strippable from the vessel's shell and processed, for example, by incineration.

Another embodiment of the invention for soil decontamination, appropriate for example in an emergency response mode where time for action is limited, provides for the host receptor matrix membrane to be applied via spray to the soil surface, thereby immobilizing and/or isolating a spill area. An electrode array could subsequently be put in place via incisions of the host receptor matrix polymer membrane, and the electropotential established. The use of the apparatus and method of the invention in an emergency response mode is anticipated for decontaminating soils which may have been contaminated, for example, by fallout from weapons testing, a nuclear accident, spills of liquid wastes, contamination from seepage pits, contaminants due to leaking drain lines, or any similar such event.

In another embodiment of the invention, soil decontamination can be achieved using a sheet type of host receptor matrix which can be supported so that it can be repeatedly repositioned over multiple contaminated soil zones. The number of repeat cycles would be limited by the ultimate saturation of the host receptor matrix to the limit of its ion uptake capacity.

The metal ion decontamination process of this invention can be carried out in-situ when the anodic and/or cathodic elements are provided within a polymer host receptor matrix and/or alternatively are positioned one relative to the other, such that the ionic species must move through the host

receptor matrix in order to approach the electrode. The electrode and polymer element can be positioned contiguous to the bulk media (either soil, water, or similar such contaminated bulk source) and at an optimum distance from each other. The optimum distance is determined by a number of variables, such as the conductivity of the soil, the electrical capability of the power supply and conductors, the depth to which contaminants have penetrated, the nature of the contaminants, and the soil type. As used herein, the term in-situ refers to a process that can be conducted at the contaminated bulk source itself, i.e., the soil or water does not have to be transported to a remote site for treatment.

The host receptor matrix may comprise an ion permeable composite, which can optionally incorporate ion immobilizing fillers, and ion conductive polymeric species which can be positioned in such a manner that the matrix is electrically "in-series" with the current flow. Additionally, the physical characteristics of this composite should be such that the host receptor matrix, once loaded with contaminants as a result of the electrical extraction cycle, has a sufficient structural integrity to permit removal and disposal of the wasteform while holding the contaminants suitably confined within the matrix.

Thus, in accordance with the invention, when a metal ion contaminated bulk source is encountered, such as a mass of soil, an anode array can be installed in a spatial arrangement and at a depth dictated by the physical characteristics of the contaminated bulk source. The polymeric host receptor matrix can be deposited over the contamination area, and a cathodic current receptor can be located to function in conjunction with the matrix. Figure 1 illustrates such an in-situ decontamination array.

In accordance with the invention as illustrated by Figure 1, a cathode array 1 can be positioned on the soil surface 3 and an anode array 2, for example, a ribbon of metal oxide coated titanium, can be installed in the ground at a suitable depth below soil surface 3, which depth depends

on the depth of contaminants in the soil. For example, if contaminants are observed to penetrate to 10 cm depth, anode array 2 would be positioned at a depth below this 10 cm contaminated zone. Alternatively, in accordance with the invention, the cathode array could be located in the soil and the anode array positioned on the soil surface. The cathode may be made of, for example, copper, steel, stainless steel or graphite. The anode may optionally be made of platinum, carbon, steel, copper, stainless steel or graphite. A polymer host receptor matrix 4 can be spray applied directly to the soil surface 3 using, for example, twin stream proportioning spray equipment. An electrical conductor (not shown) which may consist of light gage aluminum wire fabric can be installed over polymer host receptor matrix 4 to uniformly contact the membrane surface. Optionally, an electrically conductive coating 6 (for example carbon filled or conductive fiber filled) can be applied thereto to assure good electrical contact. An example of such a coating 6 employing conductive fillers is disclosed in U.S. Application No. 07/348,525 filed on May 8, 1989. This coating formulation uses graphite filler and optionally 20-30% metallic powder, more specifically comprising, for example, 30 parts deionized water, 15 parts carbon fiber and 5 parts water swellable polyurethane polymer, by weight.

An electrical power supply 8 is connected to provide, for example, a 0-100 volt D.C. electrical potential between the two electrodes. A suitable electrolyte, for example, potable water, can optionally be introduced into the soil bulk to enhance electrical current flow. Metal cations in the soil are induced by the electrical potential to move toward polymer host receptor matrix 4. The ion permeability of polymer host receptor matrix 4 is such that ions can travel into the matrix.

As an ion transgresses polymer host receptor matrix 4, it may encounter a gradually increasing pH gradient caused by the OH⁻ ion reaction at the electrode, which gradient can drive the ion to insolubility.

Another possible route is for the ion to be immobilized by reduction to some metal-like form at the cathode.

The ion has a third possible route, namely to be immobilized by an ion exchange site on a filler, such as a zeolite.

A fourth possible immobilization option is for the ion to be immobilized by the ion exchanger chelate site pendant on the electrolyte polymer.

A fifth ion immobilization option, which is viable as long as the electropotential is maintained, is for the ion to concentrate in the interstitial water domains which are created within the polymeric host receptor matrix 4.

It will be readily apparent to a person skilled in the art of metal recovery through ion exchange that the incorporation of the multiple mechanisms as described above into a single recovery process and apparatus will provide a means for ion extraction that is much more efficient in payload per unit of extractant than has heretofore been possible with prior art means.

Alternatively, the host receptor matrix can be introduced in some other configuration such as electrode/polymer matrix cylinders installed via well bores, either vertically or in some cases, horizontally in the soil. In all cases, a current flow is established between the anode and cathode, which current flow is provided by an impressed voltage that is sufficient to cause a migration of the radioactive species from the soil matrix to the host receptor matrix.

In accordance with the invention, Figure 2 depicts a vertical in-situ electrode array. Once in contact with the conductive membrane, the radioactive ions can be mobilized onto and captured by the host receptor matrix. The electrodes could be arranged in alternating polarity. In this arrangement, each anode 10 would drive ions toward cathodes 12.

The optimum distance between electrodes 10 and 12 can be determined by considering a number of factors, such as:

Soil Conductivity
Nature and Chemistry of Contaminants
Soil Chemistry
Operational Cycle Objectives
Level of Decontamination Objectives
Power Supplies Available

As described previously, the engineering design of the electrode array will generally be site specific and will consider numerous variables in arriving at an optimum anode and cathode array and the consequential electrical field and ion flow between the two electrodes.

Electrochemical Design Considerations:

There are several references that disclose the basic principles relevant to the design of the electro-extraction apparatus, namely:

Hine, F., "Electrode Processes and Electrochemical Engineering", Plenum Press, New York, 1985.

Heitz, E. and Kreysa, G., "Principles of Electrochemical Engineering", VCH Publishers, New York, 1986.

The design of the electrolyte should minimize introduction of foreign ions to avoid competing chemistry in the host receptor matrix. Moreover, the current flow should be sufficient to cause migration of target ions. Optimization of the apparatus will ultimately involve the several disciplines of transport kinetics, chemical kinetics, chemical thermodynamics, ionic mobilities, and absorption phenomena.

Those skilled in the design of electrochemical devices will recognize the fact that there are practical limits to the "reach" or range of influence of the "cell". An optimum design will take into consideration the geology, soil chemistry, apparatus installation and operating costs, project time frame objectives and such, and, based on these factors, the anode positioning, geometry and spacing can be determined. Actual dimensions will have important

consequences for mass transfer, as well as for electron transfer kinetics.

Electrode Considerations:

High surface area electrodes are generally preferred, i.e., those with a ratio of surface area to cross-sectional area greater than 3. Such high surface area electrodes have the advantage of enabling high yield. A typical decontamination application involving a cell incorporating a vertical or horizontal "well-type" electrode/polymer array can produce results that are as much as eight to ten times those anticipated for a conventional anode/cathode array. It has also been observed that electrode chemistry will affect the productivity or longevity of the overall system in this application of an electrochemical cell. Therefore, carefully selected high performance electrodes will obviously play an important role in performance. Graphite cylinders and metal oxide coated titanium are two examples of such electrodes. The selection of the polymer membrane composition can also augment the electrode performance. High conductive polymer compositions have been found to provide an improvement in operational efficiency.

It has been found by the present inventors that certain electrically conductive polymer compositions can function to displace the electrode chemical reaction such that sacrificial destruction of the metallic anode is minimized. Electrically conductive coating composites have been identified which consist of polymer/water gels which include carbon fiber fillers. Such composites can be configured so that they comprise the inner layer of the host receptor matrix and thus encase the anode, thereby ensuring that chemical reactions take place away from the metal anode surface.

The Anode:

The electrode at the anode should be constructed of a material that is not subject to rapid degradation in such exposure. Furthermore, the selection of the anode polymer can play an important role in enhancing the electrode life.

Materials such as oxide coated titanium have been found to provide viable anode materials. Where it is desirable to use less sophisticated and less costly anode materials, electrically conductive polymer materials, such as those described above, can be used to protect the anode from deterioration.

Power Supply:

The power supply, i.e., the rectifier, provides the driving potential for electrons. The electrochemical cell performs both reduction and oxidation such that every electron added at the cathode (reduction) must be balanced with the loss of an electron at the anode (oxidation). The two processes must remain in balance. The direct current passing through the decontamination apparatus causes two distinct chemical processes to occur, one at each electrode. The power supply is both a source of electrons and an electron "sink".

The best type of rectifier is one controlled by a variable transformer. A tap transformer (which has multiple taps and is controlled by switching the output connection from one tap to another) can also be utilized.

Electrolyte Preparation:

Those skilled in the art of metal extraction will realize that numerous materials are available that can be added to the bulk source to modify the chemical state of the ions to be extracted. Selection of these materials will be based on considerations such as environmental impact, efficiency of the additive in enhancing ion mobility, economics, handling characteristics, etc. The ideal electrolyte is water, both from environmental considerations and economics. Other electrolytes that are viable are liquid fertilizer solutions and liquid extractants used in chemical leachate mining operations.

The mixing facility for electrolyte preparation may consist of corrosion resistant tanks, a powered agitator, and suitable provisions for chemical inlet and outlet. In the electrical extraction process described herein, there is

normally only one electrolyte occupying the bulk space between the two electrodes. One can readily anticipate many variations where the selected electrolyte which optimizes the extraction of a specific ion at a specific voltage could, upon depletion of said specific ion, be replaced by another electrolyte to remove another ion or spectrum of ions. In yet another possible variation, the electrodes could be reversed after extraction of a first ion to extract a second ion.

Polymer Host Receptor Matrix:

The polymer host receptor matrix is a vital part of the process of the invention. The process of the invention is essentially an electrochemical process being operated in a batch mode, with the target ion complexes being withdrawn at the end of the process, leaving behind the depleted bulk source, which can optionally contain residual electrolytes. Alternatively, the ion rich bulk source near the polymer can be visualized as being depleted continuously, with fresh materials migrating from the bulk source to replace those transferred into the host receptor matrix.

There are many possible variations for achieving the desired electrode encasement of the host receptor matrix that surrounds the electrode. The host receptor matrix for such a service can consist of multiple layers of variant compositions. One of the coatings can be a electrically conductive elastomer to which a metallic mesh backing can be installed or an electrically conductive metallized polymer can be installed to facilitate the function as an electrode.

It has been discovered that the effectiveness of the process of the invention depends on the electrochemistry which takes place at the electrode during the operation of the cell and upon the ability of the host receptor matrix to both provide a functional envelope for the electrode chemistry and to reliably confine same. The structural polymer component should be, to some degree, absorptive of water (hydrophilic), without itself dissolving in the water. It should also be chemically inert to water and to

electrolytes such as salt, acids, caustic and other chemicals which are encountered at or near the electrodes. The mass polymer, when combined with the remaining constituents of the host receptor matrix, should be only slightly permeable to (ideally totally impermeable to) the counter ion species which are developed due to the applied electropotential. The term "mass polymer" as used herein is meant to describe the polymer which provides the structural integrity of the matrix.

In most instances, it is this mass polymer which is cross-linked or cured in some manner to provide the structural properties of the host receptor matrix. The structure and porosity of the host receptor matrix is determined principally by the conditions of polymerization of the mass polymer (to which ionic sites may or may not be pendant). To this mass polymer, it may be desirable to blend polyelectrolyte materials. Additionally, it may be advantageous to incorporate into the matrix, selected fillers and chemical additives, which become immobilized within the matrix.

Mass polymers prepared in the presence of major amounts of nonpolymerizable diluents (polyelectrolytes) have been previously disclosed. Macroporous ion exchange resins (sometimes referred to as "macroreticular" or "isoporous") have become prominent since about 1960. For example, in U.S. Patent No. 3,808,305, Gregor reports an interpolymer membrane of a matrix polymer, a polyelectrolyte and a cross-linker to achieve desired pore size.

It is through the proper wedding of these desired properties that a stable and functional host receptor matrix can be devised which can accommodate the buildup of the desired pH gradient while surviving its destructive potential.

Examples of materials which meet these requirements and can be used as the mass polymer component in the host receptor matrix of the invention are polymers of the following species: the epichlorohydrin-bisphenol A epoxies,

bisphenol F epoxies, vinyl esters, polyesters, the N-vinyl lactams, examples of which are N-vinyl pyrrolidone and N-vinyl imidazole; C₂-C₄ alkylene oxides such as ethylene, propylene and butylene oxides; vinyl alcohol, made as the polyvinyl alcohol by hydrolysis of polyvinyl acetate; cellophane and cellulose acetate; nitrocellulose, e.g., pyroxylin, of degree of nitration about 11%-12% N; polyurethane including emulsions or specially formulated hydrophilic species; and acrylics such as polyacrylamide and polyacrylic acid. In certain instances, emulsions of these polymers have been successfully used to form functional mass polymers.

Cross-linking is optional. Successful host receptor matrices have been made with polymers that form rigid gels solely by incorporating water within the matrix. Other successful structures have been provided by chemical cross-linking and networking of polyfunctional agents. Examples of such cross-linking agents are polycarboxylic acids such as fumaric, oxalic, adipic, maleic and phthalic acids, and certain primary and secondary amines which are reactive with polyurethanes or epoxies. Also many of the water soluble polyhydroxy compounds function both as the structural polymer matrix and as a plasticizer, for example, dimethhydroxy ethylene urea; organic di-isocyanates, e.g., hexamethylene, 2,4-tolylene, and 4,4'-diphenylmethane diisocyanate; and divinyl monomers, e.g., monomers having two ethenoid bonds (or groups) as in methylene bisacrylamide or divinyl monomers.

Where used, chemical cross-linking can be affected by direct copolymerization of the polymer and cross-linking agent in-situ. One successful matrix polymerization method provides for a hydrophilic polyurethane polymer to be added directly to an aqueous slurry wherein an aqueous gel results. Another provides for a vinyl ester and water mixture to be solidified with an initiator of ethenoid bond polymerization. Suitable initiators are benzoyl, lauroyl, and t-butyl

peroxide. Proportions of the cross-linking agent are approximately 0.1%-2% by weight of the vinyl ester polymer.

Still another advantageous matrix polymer uses a polyurethane emulsion which is cured using a blend of epoxy emulsion and hydrophilic amine, which cures to form a stable polymer and water matrix.

Still other useful matrix structures have been obtained using polyvinyl alcohol and polyvinyl butyral modified polyvinyl alcohol.

The outstanding chemical resistance of fluropolymers suggests that such polymers would also be excellent candidates for the mass polymer in the host receptor matrix.

Other examples of mass polymers include a composition by weight based on styrene as follows: styrene 100, di-vinyl benzene 2, azodiisobutyrodinitrile 4, long chain alcohol 6. To this mass polymer matrix, the ion permeable electrolyte, ion exchange fillers, organic ion exchanger and similar optional components can be added.

Another successful mass polymer composition by weight based on acrylic is as follows: N. N' methylene bis acrylamide 28, potassium acrylate 10, acrylamide 80, dimethylaminopropionitrile (DMAPN) 1.8, ammonium persulfate 1.0. This composition has inherent ion exchange properties which can be supplemented with the optional components as described above.

One embodiment of this invention relates to a host receptor matrix wherein the mass polymer comprises a porous ceramic membrane element manufactured of metal oxides, primarily alpha alumina (membralox manufactured by Societe des Ceramiques Techniques). The cylindrical membrane (7 mm-internal diameter and 10 mm outside diameter, for example) can be end-sealed with impermeable epoxy polymer and filled with a cation exchange bead such as GT-73 (Rohm & Haas), allowing a suitable void space for bead expansion. A graphite electrode can be installed in the center of the ion exchange media and rigidly fixed via an impermeable polymeric material. The result is a rigid cylindrical element

constituting a host receptor matrix which surrounds the electrode.

Another ceramic class mass polymer useful in the present invention is an open cell glass foam matrix formed by a mixture of alkali silicate, a surfactant and sodium silica fluoride. To form a suitable host receptor matrix, the foam is impregnated with a polymer such as polyisoprene and the resulting composite is sulfonated using techniques disclosed in U.S. Patent Nos. 3,613,957 and 4,071,546.

One skilled in this art will understand that the interior annulus of the ceramic membrane element can optionally be filled with the ion exchange media as described, and that the media that is used for filling the annulus between the electrode and ceramic exterior shell or host receptor matrix can be soluted from a vast array of materials, either ion exchanging or ion immobilizing, acid polymers and similar, to achieve the optimum performance in ion immobilization for specific uses.

Another embodiment of this invention involves a host receptor matrix which comprises an exterior matrix consisting of melt blown polypropylene fibers formed into a cylindrical element. The cylindrical element (15 mmOD and 14 mmID, for example) can be sealed at base with an impermeable epoxy polymer and a graphite electrode can be installed in the center. The interior annulus can be filled with an ion exchange bead material such as GT-73. The graphite electrode is preferably rigidly fixed and the exterior top surface is preferably sealed via an impermeable polymeric material.

There are several optional elements that can be added to the mass polymer to form the host receptor matrix. One is the fixed charge ion conducting polymer (polyelectrolyte) which can be incorporated into a host receptor matrix to provide electrical conductivity via current carried by similarly charged ionic species that travel along the pathways provided by the polymer's fixed counter ion receptor sites. Furthermore, under the proper conditions, these fixed charge sites can provide the requisite ion immobilization

which is an ultimate objective of the invention. The composite described herein is unique in that both these properties can be achieved by a polymer alloy which is formed in a composite that comes directly from an aqueous phase which is never dried during its processing. In one embodiment, the casting solution includes a matrix polymer, a polyelectrolyte and optionally a cross-linker. When the matrix material cross-links to a stable structure, the microstructure consists of a network of ionic transport sites whose function is to enhance charge transport through the matrix. The composite has yet another unique characteristic, namely the fact that the electrode can function as an integral part of the host receptor matrix. This composite host receptor matrix configuration provides yet another novel aspect when it functions as an element of an in-situ bulk media decontamination unit.

The mechanism for ion conduction by polymers is a complex phenomenon. Although applicants do not wish the invention to be limited to any theoretical mechanism, one explanation of the mechanism of ionic conduction, which has been proposed for the analysis of the interaction of a polyethylene oxide-alkali metal complex, is that the phenomenon is dependent on a pendulum-like movement within the elastomeric phases of the polymer. This movement is postulated to be strongly dependent on the freedom of movement (for cooperative rearrangement) of polymer segments, and on the associated local free volume. It is theorized that this movement allows the cation to be passed from an adjacent counter ion site, and thus accounts for the migration along the polymer's length.

It can be concluded from such a theory that optimization of the ion conducting polymer matrix material can be achieved by working with the solvating polymers involved in the matrix.

Such analysis could explain the generally accepted belief that the use of plasticizers helps to reduce the glass

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transition temperature (T_g) of the polymer and hence improves the conductivity of the polymer electrolyte.

Another mechanism that may contribute to determining the ion conductive property of the polymer electrolyte is the ligand or anion receptor site. Scientific literature is filled with extensive explanation for possible behavior. For example, the use of amine functions favors cation coordination with alkali metals because of the amine nitrogen. Specifically, the donor number (DN) for triethylamine is 61, versus a DN of 20 for tetrahydrofuran or 14 for polyethylene oxide. This would lead one to believe that such an amine functional polymer would be a candidate for alkali metal ion transmission. The strong similarity between such amine polymers and crown ethers confirms the theoretical hypothesis since the fully nitrogenized cages of the crown ether are used as complexing agents for alkali metals.

The ionic host receptor matrix is essentially an ion trap. One of the optional elements of the receptor matrix, the ion exchange polyelectrolyte, contributes to the ion transmission and ion immobilization properties. While the ion exchange sites on this polyelectrolyte are important, especially in achieving ion transmission, the decontamination process accommodates a substantial range in the type of ion exchange sites which can be incorporated in the receptor polymer composite. The desired function is realized via use of these conducting polymers, otherwise called "aprotic" polymer electrolytes, which are a class of ion conduction materials useful for electrochemical processes.

A candidate material for the polyelectrolyte found in "inimically-conducting" polymers is the so-called conjugated unsaturated polymers. The most successful results were found in a family called charged polymers and polyelectrolytes. Charged polymers are salt-bearing solvating polymer complexes known to be a solid solution of salt in a polymer. Their electrochemical performance is essentially the same as that of a liquid electrolyte.

A preferred class of polymers called polyelectrolytes are polymers that bear their own ion generating groups chemically bound to the macromolecular chain. The presence of a counter-ion maintains the electro-neutrality. An example is polystyrene sulfonic acid or polystyrene sulfonate.

Acid functionality is a desirable feature in the host receptor matrix used at the cathode. Examples of polymer acids having such a feature are: polyethylene imino acetic acid, molecular weight 50,000-100,000 (PEI-1000 from Dow Chemical); heptadecyl phosphoric acid HDPA $C_{17}H_{36}OPO(OH)_2$; poly sodium vinyl sulfonate; and polystyrene sulfonic acid.

The weakly acidic polymers such as polyacrylic acid are relatively non-adsorbing and act as a cation permeable polyelectrolyte in a highly alkaline environment.

Another example for developing a matrix of well controlled ion permeability involves a urea formaldehyde mass polymer combined with a sulfonated poly styrenated naphthalene polyelectrolyte, having a filler material which is a synthetic zeolite of the clinoptilolite family.

In contrast with the prior art technology, which provided either ion permeation or ion immobilization, the host receptor matrix of the invention functions to provide an ion permeable medium functioning within an ion immobilization matrix. The polymer host receptor matrix functions in a manner that could be described as analogous to ion chromatography. In the initial operation, the outermost region of the host receptor matrix and electrode composite functions as an ion transport media. While functioning in this mode, the composite provides a one-way ion flow which is well known in the prior art and which is essential in electrodialysis phenomena. Because the matrix restricts migration of the counter ion (the anion) as the cation moves deeper into the polymer matrix, it experiences a continuous gradient of steadily increasing pH. Ions which are prone to form insoluble salts when they combine with an anion experience such an opportunity to form an insoluble complex.

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This tendency of positively charged ions to form insoluble salts upon contact with an anion can be enhanced by the use of additives such as reducing solutions which may consist of aqueous hydrogen sulfide, ammonium thiosulfate or a thiocarbonate such as "thio-red", manufactured by Eniromental Technology of Sanford, Florida. The immobilization of the complexed salt is achieved by the exchange sites associated with the polymer or alternatively by ion exchange fillers such as zeolites, clays, or vermiculites. It is observed that no escape of ions from the host receptor polymer matrix is likely, because the backward migration will return the salt to a solubilizing region whereupon it will be resolubilized and the ion will again be influenced by the electrical field which will transport it back to the insolubilizing region.

In the case of a cation which can be reduced at the cathode, for example copper, the metal ion may migrate under the electrical gradient, steadily proceeding through the cation permeable composite, and ultimately reaching the electrode, where it can plate out as metallic copper.

In the case of the hydrogen cation, the path is the same, with an ultimate release of hydrogen gas upon reduction at the anode.

The anode reaction can provide a similar means for ion mobilization and reception, albeit for oppositely charged species.

Filler Incorporated in the Host Receptor matrix:

Ion exchange fillers have been found to be effective when incorporated into the host receptor matrix. Such fillers can be optimized to selectively ion exchange with specific radioactive ions. For example, in a treatise on ion exchange separations with molecular sieve zeolites, presented by John D. Sheryan at the 83rd National Meeting of the American Institute of Chemical Engineers, methods were presented for selective exchange of cesium, strontium and magnesium, among other metals. In this invention, the target radioactive ions are transported into the polymer host

receptor matrix which incorporates such fillers, whereupon they are exchanged and thence held tightly to the solid ion exchanger. Optionally, an organic resin possessing the desired selectivity can be incorporated. In the present invention, the fine particle size requirement, which is critical in normal diffusion controlled ion exchange, is not so important. Typical organic polymer ion exchange particles will be supplied in sizes ranging from 16 mesh to about 200 mesh. The fine mesh particles which would be highly preferred in the prior art applications (for increased surface area as described hereinabove) are not so essential for this invention due to the fact that the electrochemical potential will compensate by dramatically enhancing the ion uptake rate. Also, the larger particles simplify the confinement (immobilization) of these particles which is especially important, once they are contaminated.

Another example of a highly selective immobilizing filler material is potassium cobalt - hexacyanoferrate, which is extremely selective for cesium.

One embodiment of the invention provides a sheet-type host receptor matrix that incorporates an ion exchange cloth similar to that commercially available from Carborundum Corporation under the designation of "Ion Exchange Cloths and Felts" or ion exchange products marketed by Scott Paper Company under the designation "Industrial Foam Ion Exchanger". These can be useful in this process when properly assembled in the electrochemical array which is described in this disclosure. Said ion exchange cloths can be used alone or as a single element of a multi-element composite. Cellulose fabrics and similar such ion exchange media can be used.

It is important that the electrode used with such an ion exchange cloth should be configured so as to provide a uniform current through the cloth and an electrolyte solution should be provided such that the ion transmission can be maintained through the cloth. These forms can be relatively

easily deployed over the contaminated area, easily fitted with electrode membrane, and would be recoverable.

When the polymer host receptor matrix of the selected geometry is not in itself sufficiently impermeable to the counter ions, that is, is insufficient in electrolyte exclusion, the membrane may be combined with a thin exterior layer which is less permeable to the ions in the bulk. Superficial layers that may be applied to the matrix can be either in the form of the free acid or its sodium or other alkali metal salt; quaternary and tertiary amine derivatives of polyvinyl aromatic C₆₋₉ hydrocarbons such as polystyrene, polyvinyl toluene, and polyvinyl xylene, in which the group -CH₂ - N(CH₃)₃Cl, for instance is attached to a carbon of the aryl rings; melamine formaldehyde resins (e.g., 50%-70%) admixed with guanidine (30%-50%); and polyacrylic or polymethacrylic acid.

Depending on use and processing constraints, thickness of the ion impermeable coating can range from 25 to greater than 10,000 microns.

The bulk source contacting layer of the membrane may be applied in any usual manner, such as by casting a dual stream matrix; by spraying a solution of an HRM consisting of a hydrophilic polymer such as a modified polyurethane or polyvinyl alcohol, suitably filled with polyelectrolyte and/or ion scavenging fillers. Optionally, the functional membranes can be made by treating an as-cast polymer matrix using SO₃ gas by techniques described in U.S. Patent No. 3,647,086.

Optionally, the sulfonation of a polymer matrix, such as polystyrene, can be made in the usual manner as, for example, applying over the polymer in film form, a solution of sulfur trioxide-triethyl phosphate complex in dichloroethane or other volatile organic solvent therefor, subsequently evaporating the volatile solvent, and then washing out remaining soluble material with ethanol followed by water, to give the finished composite membrane. As the sulfonic acid derivative so made is used in contact with a metal salt, such as sodium chloride in sea water, the acid

converts to the metal sulfonate. Fuming sulfuric acid can be similarly used to sulfonate an organic polymer, through its unsaturated sites.

Plasticizers can also be used to control the degree of cross-linking and to control or modify the polymeric network structure and porosity of the matrix.

The same material can be used for the plasticizing effect. This dual purpose material, after serving as the plasticizer during formation of the membrane, serves as the pore former which defines the domains which are occupied by interstitial water reservoirs. Examples of such bifunctional components are water, dextrose, sucrose, and other sugars; water soluble polyhydroxy alcohols such as glycerol and ethylene, propylene, and polyethylene; and polypropylene glycols and their water soluble ethers and esters, e.g., the monoethyl ether monoacetate of ethylene glycol, such as "Cellosolve" acetate; formamide and acetamide; mono-, di-, triacetin; diacetone alcohol; and like non-ionic materials.

It is anticipated that the development of the host receptor matrix will consider a multitude of physical properties to arrive at an optimum design for a specific application. For example, potential for recycling the matrix may not be a vital consideration when cleaning up a small spill area, such as contamination near a laboratory waste receptacle. On the other hand, a major nuclear plant accident, such as Chernobyl, involves decontamination of a massive land mass, and a recyclable host receptor matrix is essential.

Those skilled in the art will recognize that there is a wide variation in the types of contaminants encountered as well as in geological conditions and migration patterns. An effective host receptor matrix/electrode array must take into consideration this multitude of factors.

Electrode polarization introduces an additional variable to the process. The literature includes numerous references dealing with this phenomenon. For example, the electropotential can be reversed for an interval sufficient

to destroy the polarization effect, then restored. Alternatively, the host receptor matrix can include chemical additives which will resist the electrode polarization effect. It is envisioned that such additives can be selectively added to the polymer layer adjacent the electrode.

The following Examples are provided to illustrate various embodiments of the invention. The Examples are not intended to limit the scope of the invention.

Index
to
Examples

| Type of Bulk Medium | Description of Process |
|------------------------------|---|
| 1. Groundwater | Cation Capture in HRM at Cathode Only (Bare Titanium Anode) |
| 2. Soil | Cation and Anion Capture From SRL Soil |
| 3. Groundwater | Extended Distance Cell |
| 4. Groundwater | Anion Capture & Cation Capture in Two HRMs |
| 5. Soil | Use of Fertilizer-Extractant/Electrolyte to Clean Y-12 Soil |
| 6. Chemical Solution Cleanup | Comparison of HRM Versus Diffusion into Conventional Ion Exchange Beads |
| 7. Chemical Solution Cleanup | Ceramic Cylinder Concept |
| 8. Groundwater | Ceramic Foam Matrix Impregnated with Sulfonated Polyisoprene |
| 9. Groundwater | Electrically Conductive Polymer to Mitigate Attack on Anode |

Example 1

The laboratory scale electropotential/polymer immobilization cell illustrated in Figure 3 was used to model the process in a simulated cleanup of an underground aquifer. The anode 20 consisted of an iridium oxide coated titanium mesh (2 inch by 2 inch by 0.06 thickness). A water swellable polyurethane polymer filled with 30 percent of its weight with a cation exchange resin bead GT-73 by Rohm & Haas, and 200 percent of its weight of water comprising the host receptor matrix (HRM) 22 was cast over the cathode electrode to provide complete encapsulation of the immersed portion of the cathode 24, a graphite rod 1/8 inch diameter by 3 inches long. The water 26 to be treated was placed in a stainless steel tank 28. This water solution was designed to simulate the water composition in a large contaminated aquifer. This container held 10.1 liters of the synthetic aquifer water. Table 1 describes the water conditions at the start of the test. The input electrical power was established via a remote power unit 30 which was connected as shown and an electrical potential of 10 volts D.C. was impressed. A good correlation of power demand was observed in comparison to that estimated by the following relationship:

For each faraday of current, one equivalent of H⁺ ions will migrate from the direction of anode to cathode, ultimate being given up by the water to the polymer composite to subsequently travel through the ion permeable composite, (the catholyte) continuing in the direction of the cathode. Correspondingly, one equivalent of OH⁻ ions is oxidized and released as gaseous O₂ at the anode, and a total of one equivalent of H⁺ ions as well as any combination of migrating bulk media ions, Fe⁺⁺, Mg⁺⁺ or Co⁺⁺, etc., can be immobilized at the cathode.

While the hydrogen ion concentration was high (i.e., the low initial pH) in the polymer composite, most of the

cathode reaction involved H⁺ ions reduced at the cathode and power demand was higher, i.e., 50ma. However, as the pH rose to a value of about 6, as the result of hydrogen liberation, (and OH-ion generation) current flow was observed to diminish to approximately 15 ma. Metal ions appeared to codeposit, as hydrogen was evolved, at the cathode in the form of metals. At the same time, migration of OH-ions away from the electrode was noticeably inhibited by the polymer matrix, which contributed to a pH rise in the polymer, the highest pH being immediately adjacent the cathode. This high pH caused some of the ions, notably iron, to precipitate in the polymer as hydroxides. The charge neutrality requirement across the bulk electrolyte was ultimately maintained via a counter-ion flow back to the anode, and subsequently with the release of oxygen at the anode. The theoretical current flow under a voltage potential was estimated using the above described relationships and predicted was a current flow of approximately 15 ma for the above described setup.

Cleanup of this simulated underground aquifer was the ultimate objective for this apparatus. The aquifer water was modeled after a large aquifer contaminated with various ionic species. (See to the composition shown in Table 1).

The 10 volts D.C. applied electropotential represents a scale-up potential of 13.3 volts/meter for this aquifer. The basis for this voltage presumed an electrode spacing of about 15 meters, and an electropotential of 140 volts. The 10 volts D.C. potential was maintained for 48 hours, during which several water samples were taken. These water samples were analyzed for the various ionic species. The current was also monitored and its value stabilized at approximately 15 ma through the duration of the test.

In addition to the demonstration of cleanup of the ground water, this example permitted the observation of three controllable parameters which influenced the limiting current demand for this process. (1) The concentration of reducible species at the cathode or oxidizable species at the anode which can be eliminated through the selection of an

electrical potential above the decomposition potential of water. The water, therefore, provides an ample supply of electroactive species. (2) Electrodes with large surface area or high efficiency toward the electrode reaction are preferred. This prevents the electrodes from limiting the ion pickup. For this example, a porous graphite cathode (as opposed to bare stainless rod), and an anode with an oxide coating that promotes a high efficiency was used. With these variables controlled, the ionic mobility becomes the controlling factor. (3) The current becomes dependent upon electrode spacing, applied voltage, and ionic concentration where the ionic concentration in this instance is dictated by the aquifer composition.

Table 1

| <u>Analysis of Water Samples</u> | | | |
|----------------------------------|------------------------------------|---|--|
| Element | Concentration At Start (ppm) | Concentration After 48 Hrs. (ppm) | Concentration After 160 Hrs. (ppm) |
| Manganese II | 5.73 | 5.08 | 1.13 |
| Cadmium II | 1.11 | 1.01 | 0.25 |
| Iron III | 6.50 | 0.79 | 0.02 |
| Lead II | 6.93 | 8.83 | 0.12 |
| Fluoride | 6.70 | 9.40 | 10.2 |
| Sodium | 279 | 277 | 280 |

Example 2

Figure 4 shows the laboratory apparatus which was utilized to carry out the electropotential extraction and polymer immobilization process to decontaminate a sample of soil retrieved from a seepage basin of a large industrial complex.

The sample consisted of approximately 4,000 grams of naturally dampened soil, whose radiological and toxic metal components are described below.

The soil 40 was placed in a two inch diameter by twenty four inch long plexiglas tube 42. Tube 42 was fitted on the bottom with a loosely fitting plexiglas end cap 44 suitably penetrated by an electrical conductor 46 which in turn was attached to a ruthenium oxide coated titanium screen mesh 48. The connection/junction 50 between electrical conductor 46 and screen mesh 48 was covered by an epoxy sealant to prevent destruction by sacrificial corrosion. The anode host receptor matrix 52 consisted of a two layer polymer sandwich, the first layer consisting of an anion exchange resin bead immobilized in a water swellable polyurethane matrix polymer, and the second layer consisting of an unfilled water swellable polyurethane water gel. The top of the laboratory apparatus included a cathode host receptor matrix 54 comprised of a water swellable polyurethane polymer, filled with a naturally occurring zeolite filler (TSM140 H). See Table 2A below for polymer composition.

Table 2A

| <u>Composition of Host Receptor Matrix</u> | |
|---|---|
| <u>Anode</u> | <u>Cathode</u> |
| D.I. Water - 20 grams | D.I. Water - 20 grams |
| Ion Exchange Beads - 15 Grams (Strong Base Type) | Zeolite - 15 grams TSM-140 H |
| Water Swellable Polyurethane Polymer- 6 grams | Water Swellable Polyurethane Polymer-6 grams |

The anode polymer was preconditioned by immersion in 0.1 molar nitric acid for 20 hours during which time a D.C. potential of 20 volts was imposed via a stainless steel

electrode pressed into the composite. A plastic end cap 56 provided support for a stainless steel cathode 58 pressed into the host receptor matrix 54. Plastic end cap 56 also provided support for stainless steel cathode 58 which was ultimately connected via electrical conductor 60 to a D.C. power supply. Approximately 100 ml of ammonium phosphate fertilizer was added to enhance electrical conductivity. The above described cell was operated at 40 volts D.C. and approximately 1 milliampere current load for a period of 7 days. During this time, distilled water was added to the soil periodically to maintain the soil in a moist state. The pre-remediation soil assay data are presented in the following Table 2B:

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Table 2B

| <u>Soil Sample Assay</u> Concentration of Metal Ions Before Remediation | |
|---|-------------------------------|
| Element | Concentration in P.P.M. |
| Calcium | 19.0 |
| Magnesium | 3.7 |
| Manganese | 2.1 |
| Lead | 0.2 |
| Zinc | 2.0 |
| Aluminum | 49.0 |
| Boron | 0.6 |
| Iron | 36.0 |
| Sodium | 5.0 |
| Strontium | 0.13 |
| Titanium | 0.2 |
| Vanadium | 0.6 |
| Phosphorus | 3.1 |
| Silicon | 4.9 |
| Mercury | 0.015 |
| Uranium | 0.03 |

After remediation, an analysis was performed of the soil sample, focusing on the two elements of primary concern from a toxicological standpoint, mercury and uranium. Mercury and uranium removal was virtually complete, i.e., below instrument detection limits. Analysis of the two polymer composites revealed:

In Anode Polymer

Cadmium
Cobalt
Copper
Magnesium
Iron
Chromium
Mercury
Uranium
Lead

In Cathode Polymer

Manganese
Barium
Sodium
Strontium
Titanium
Aluminum
Calcium

Not Detected in Either Polymer

Zinc
Vanadium
Boron
Phosphorous
Silicon

Example 3

The ion mobility characteristics as well as the range of influence of the electropotential-induced ion migration into the immobilizing polymer was characterized using a specially designed cell shown in Figure 5. The apparatus was filled with the groundwater solution described in Experiment No. 1. A polyvinyl chloride tubing array 70, approximately 10 ft. long by 1 and $\frac{1}{2}$ inches diameter was provided with fittings 72 to permit introduction of electrodes and introduction of water.

Electrodes consisting of a cathode 44 made of graphite and an anode 76 made of ruthenium oxide coated titanium were encased in the cathode host receptor matrix 78 and the anode host receptor matrix 80 as described in Table 3A. A center

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opening 82 was incorporated to permit optional sampling at this point. The groundwater solution 84 was introduced into the apparatus and the negative pole of a D.C. power supply was connected to the cathode 74 and the positive pole to the anode 76.

Table 3A

| Anode HRM Composition | Cathode HRM Composition |
|-----------------------|-------------------------|
| 20 grams D.I. Water | 20 grams D.I. Water |
| 15 grams Strong Acid | 15 grams Syloid Znl |
| Resin Bead | 6 grams Flexrock |
| 6 grams Flexrock | 5 grams Boric Acid |

Flexrock™ is a water swellable polyurethane polymer

Syloid Znl is a synthetic zeolite of the chabazite family

The ionic species studied were characteristic of the ions found in a contaminated aquifer in a large industrial complex. Electrical instrumentation was provided for accurately tracking voltage that had to be applied and the time needed for cleanup for a distant electrode spacing. An attempt was made to predict the rate of transport of ions based on tables of ionic conductance (from the Handbook of Chemistry). It was found that actual ionic mobility differed from the calculated values. Two contributing sources for this discrepancy are believed to be: (1) the existence of the metal ions in complex ionic form; and (2) a threshold change which occurs in transport of the ions due to the use of high voltages (Wien effect). In this instance, both anode and cathode were encased in a water swellable polyurethane matrix incorporating suitable fillers (see table). These were placed in the cell after the addition of the simulated aquifer water, which was a 10 fold concentrate of the

normally occurring aquifer water. An electrical potential of sixty volts D.C. was applied to the cell. After 96 hours, a liquid sample was taken at both ends of the cell.

Results from the experiment showed that the ions migrate as expected.

The electrolyte composition before and after the remediation program are described in Table 3B below:

Table 3B

| <u>Water Chemistry Conditions - Simulated Groundwater</u> | | |
|---|----------------------|---------------------|
| | Before Treatment PPM | After Treatment PPM |
| Manganese | 58 | 2.58 |
| Cadmium | 1 | .043 |
| Iron | 260 | .591 |
| Lead | 8 | .022 |
| Fluoride | 155 | <5. |
| Sodium | 1640 | 260. |

Example 4

The same laboratory setup described in Figure 3 of Example 1 was repeated except that the anode was configured so that the host receptor matrix (HRM) encased the oxide coated titanium electrode. The composition of this anode polymer was 30 percent by weight of weak base anion exchange resin beads, 55 percent by weight water, and 15 weight percent of water swellable polyurethane polymer. This composite was cast over the metal oxide coated titanium anode mesh which had been formed into a cylindrical rod. The anode polymer host receptor matrix provides a means for immobilizing the anion species, for example, nitrate ion and simultaneously to immobilize any ionic species in the form of

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anionic complexes. Such anionic complexes are suspected to represent a substantial inventory of metals which are observed in aquifer water. The aquifer water, the power supply and confinement tank were all comparable to Example 1. The cathode polymer host receptor matrix and graphite electrode were similar to Example 1 except that a filler was incorporated into the cathode polymer consisting of a natural zeolite TSM 140 H. The two electrodes were spaced 0.75 meters apart in a container containing 10.1 liters of the synthetic aquifer water. 10 volts was applied for 48 hours and water samples were taken as in Example 1. The results are presented in Table 4 below:

Table 4

| <u>Analysis of Water Samples</u> | | | |
|----------------------------------|------------------------------|-----------------------------------|-----------------------------------|
| Element | Concentration At Start (ppm) | Concentration After 20 Hrs. (ppm) | Concentration After 68 Hrs. (ppm) |
| Manganese II | 4.50 | 4.52 | 1.82 |
| Cadmium II | 0.946 | 0.890 | 0.351 |
| Iron III | 7.67 | 3.13 | 0.08 |
| Lead II | 12.89 | 8.62 | 3.14 |
| Fluoride | 4.70 | 3.38 | 3.77 |
| Chloride | 411.0 | 246.0 | 92.77 |
| Sodium | 238.54 | 222.74 | 46.90 |

Example 5

The materials, procedure and equipment of Example 2 were employed except that the anode polymer composite was removed and the entire laboratory apparatus was placed inside a 3500 ml glass beaker.

The clearance of the loosely fitting plexiglas end cap 44 in Fig. 4 permitted the introduction of a fertilizer

solution (ammonium phosphate) which would flow past the cathode 58 and into the soil column.

In order to preclude a too rapid permeation of the fertilizer electrolyte through the soil column, approximately 600 ml of D.I. water was added to the annular space between the glass beaker walls and the laboratory apparatus.

The apparatus was filled with a soil classified as a "mixed-water" due to the presence of both EPA classified hazardous components (primarily mercury) and a radioactive complement (primarily uranium). This soil sample had been excavated from a contaminated landfill operated by a large industrial complex.

The analysis of the untreated soil in PPM was as shown in Table 5A:

Table 5A

| | |
|-----------|--------------|
| Mercury | 1000 PPM |
| Uranium | 160 PPM |
| Barium | 20 PPM |
| Copper | Not reported |
| Magnesium | Not reported |
| Nickel | Not reported |

Prior to addition of approximately 2000 grams soil to the laboratory apparatus, the soil was pre-dampened with 125 ml of ammonium phosphate fertilizer solution. The cathode polymer, cathode and plexiglas end fitting were installed and an additional 125 ml of fertilizer solution were added to the space above the cathode and allowed to leak past the end cap and into the soil cylinder.

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An electropotential of 50 volts D.C. caused a 190 ma current flow in the cell. After 2 hours operation, an additional 200 ml of fertilizer solution was added via leakage through the plexiglas end fitting, and voltage was reduced to 4 volts D.C., with corresponding current flow of 5 milliamperes. This electropotential was maintained for 12 hours.

At the end of this period, the water surrounding the anode portion of the cell was observed to have taken on a distinct light blue coloration.

Analysis of the water from this region of the cell was as shown in Table 5B:

Table 5B

| | |
|---------|---------|
| Mercury | 32 PPM |
| Uranium | 4 PPM |
| Copper | 44 PPM |
| Barium | 3.8 PPM |
| Nickel | 1.5 PPM |

The migration of these species of normally cationic metals toward the anode would not be expected unless one takes into account that anionic complexes are likely to be encountered. Such formation becomes especially prevalent with the phosphate electrolyte solution being present.

Those experienced in soil decontamination will recognize that this extraction technique is more effective than a soil washing or chemical extraction process, which depends solely on diffusion kinetics.

For comparison, a similar quantity of soil was exposed to the same electrolyte chemistry, but with no

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electropotentials. At the end of the 14 hour contact time, there was no perceptible color change in the bulk liquid.

Example 6

A comparison of the relative effectiveness of electropotential migration and polymer immobilization phenomenon versus conventional diffusion was illustrated by comparing uptake of identical weights of ion immobilizing media under four different conditions.

In all instances, this involved a nuclear grade mixed bed ion exchange bead of a type routinely used in industrial service supplied by Rohm & Haas (XE 604). Four 300 ml beakers were cleaned and each was filled with 200 ml of a 0.05 molar solution of cobalt nitrate. Each test incorporated the same mass of ion exchange media (6 grams). In each case, the bead was placed in contact with the bulk cobalt nitrate solution, via a different mechanism. In the first instance, the bead was cast into a cylindrical form wherein the bead was immobilized using a mass polymer consisting of a water swellable polyurethane polymer. The approximate dimensions of this cylinder were 3/4 inch diameter by 2 inch length. In the second instance, the matrix ion exchange media and mass polymer media were similar in composition and geometry to the first except the center of the composite (HRM) was hollowed and filled with a buffering solution consisting of approximately 5 ml of a 10 percent acetic acid solution. For the third test setup, the resin bead was confined within a porous melt blown polypropylene mass polymer matrix whose dimension was also approximately 3/4 inch diameter by 21 inches long. In the fourth test setup, the ion exchange bead was not confined nor was it encompassing an electrode, but was instead poured into the liquid containing beaker. A graphite electrode was inserted in the center of each of the cylindrical arrays of the above three described HRM composites. The cylindrical electrode/HRM arrays were placed in containers previously filled with the cobalt solution. A counter electrode of ruthenium oxide coated titanium mesh was positioned 2 inches from the HRM. A

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potential of 10~volts was applied for 20 hours. At the end of the contact period, the four solutions were analyzed for cobalt and their results are listed below in Table 6:

Table 6

| Run# | No. of Grams of Ion Exchange Bead | Composite Wt. Mass Polymer & Water Ion Exchange Bead | No. of Grams Cobalt Extracted | Voltage D.C. | Type of Mass Polymer |
|------|-----------------------------------|--|-------------------------------|--------------|------------------------------------|
| 1 | 6 | 16.4 | 0.099 | 10V | Polyurethane |
| 2 | 6 | 16.8 | 0.239 | 10V | Polyurethane with Acid Electrolyte |
| 3 | 6 | 9 | 0.287 | 10V | Melt blown Polypropylene Fiber |
| 4 | 6 | 6 | 0.155 | N/A | None |

The test setup incorporating the porous polypropylene mass polymer and electropotential induced ion migration had the best cobalt removal. The buffered cell also performed better than the free resin bead. From these results, it was apparent that the electro-extraction process provides more effective ion capture than does normal diffusion into an ion exchange resin bead. The relatively poor performance in Run #1 illustrates a kinetics phenomenon which should be avoided in designing an effective decontamination cell. Such an arrangement tends to result in depletion of the ion transporting water electrolyte at or near the electrode surface, compromising the electro-reduction reaction and

consequently the ingress of ions into the polymer. This phenomenon is believed to be related to a high resistance to ion transmission which brings about a breakdown, or electrolytic decomposition, of water. Hydrogen is evolved and the interface between the polymer and electrode dries out. Additional drying of the overall composite results from a competing water-absorption by the resin beads. In a second observation, it was apparent that in any application involving heavy metal or radionuclide metal scavenging, the more accepted sample would be the buffered HRM (as opposed to porous polypropylene) because of the diminished chance of leaching of removed products back into the cleaned solution.

Example 7

Figure 6 depicts a laboratory scale model of an apparatus to be used for in-situ ground water remediation consisting of a host receptor matrix where the mass polymer consists of an inorganic polymer bound ceramic matrix 90 consisting of metal oxides, primarily alpha-alumina filled porous media having a nominal pore size of 1000 angstroms. Ceramic matrix 90 was a tubular element of 7/16 inch diameter with 1/16 inch wall thickness cut to a 3 inch length and the bottom was end sealed with a two part epoxy casting end cap 92. When epoxy end cap 92 was sufficiently hardened, a 1/3 inch diameter stainless steel electrode 94 was positioned in the center of ceramic matrix 90 and a mixed bed ion exchange media 96 (a nuclear grade resin available from Continental Water Systems, Metairie, La.) was poured into the annulus. The laboratory apparatus was placed inside a 300 ml glass beaker 98 which was in turn filled with 200 ml of 0.05 molar cobalt nitrate solution 100.

The anode for this arrangement consisted of a ruthenium oxide coated titanium mesh.

Five milliliters of a one percent solution of acetic acid in D.I. water was added to the annulus area of the bead-filled ceramic cylinder, and an electropotential of 10 volts D.C. was maintained for 20 hours. At the completion of this

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interval, test of the bulk solution showed a cobalt depletion of approximately 0.010 grams.

In a repeat of the above cycle, all of the test parameters remained the same, except that the bead type ion-exchange was replaced with a liquid polystyrene sulfonic acid polymer electrolyte, molecular weight approximately 5,000.

The ceramic matrix 90 confined the liquid polymer electrolyte with no observed leakage. After 20 hours operation at 10 volts D.C., a sample of the bulk solution showed a cobalt depletion of 0.130 grams.

Example 8

Structural integrity, dimensional stability and enhanced ion transmission rates were achieved by using an open cell glass foam receptor matrix to provide the structural host in the HRM composite.

A 2" x 2" x 6" open cell glass foam briquette (manufactured by Bioglas, Inc., San Antonio, Texas) was immersed in a two percent solution of polyisoprene latex and allowed to remain so immersed overnight to insure a thorough impregnation of the entire porosity of the foam. The impregnated glass foam was then dried by placing it in a warm circulating air oven overnight. Microscopic examination of the dried composite showed that the composite had retained its open pore structure, yet the glass surface 112 was uniformly covered with the polyisoprene polymer 114.

The composite was subsequently placed inside a desiccator, the bottom of which was covered with fuming sulfuric acid. The desiccator was allowed to remain sealed for 24 hours whereupon the SO₃ vapors reacted with the unsaturation sites of the polyisoprene polymer, converting same to sulfonate groups.

At the end of the vapor contact period, the composite was rinsed with deionized water to remove any leachable impurities. The resulting glass foam/polymer electrolyte composite was utilized as the host receptor matrix 116.

A carbon rod electrode 118 was inserted into the glass foam/polymer electrolyte host receptor matrix 116. This

device was then immersed in a water solution 120 which contained the following composition of metal ions in solution in ppm:

| | |
|------|------|
| Mn++ | 58 |
| Cd++ | 1 |
| Pb++ | 8 |
| Fe++ | 260 |
| Na+ | 1640 |
| F- | 155 |

An anode 122 consisting of a ruthenium oxide coated rod was placed in contact with the water solution 120, and the two electrodes operated at an impressed electropotential of 10 volts D.C.

At the end of 72 hours of operation, iron was found to have collected in cathode host receptor matrix 116. The absence of precipitation outside polymer host receptor matrix 116 demonstrated that cathode chemistry was confined to the matrix. The expected deterioration of the cathode polymer was limited to the area adjacent to electrode 118 due to the high pH generated by the cathode reaction.

Example 9

The technique for protection of the metal anode electrode with an electrically conductive polymer layer was demonstrated by means of two ion extraction cells.

These cells were similar except that one cell incorporated a 2 layer polymer HRM, with an inner layer of electrically conductive carbon-filled polymer in contact with the anode. The function of this electrically conductive layer is to displace the electrochemical reactions, which would normally be expected at the anode surface, to a location far enough away from the stainless steel electrode such that the sacrificial attack is minimized.

Cell Design:

- All Electrodes - Stainless Steel
- Voltage - 20 VDC
- Both cells were operated at: 20 Volts D.C.
- Current demand: 100 Milliamperes (Control)
- 80 Milliamperes (Conductive Polymer)
- No cathode HRM was used.

Control:

For the anode HRM, 30g of D.I. water was mixed with 5 grams of water swellable polyurethane polymer. Into this polymer was inserted a stainless steel rod. This functioned as the "control setup".

Conductive Polymer:

In the other setup, the HRM polymer consisting of 30g of D.I. water mixed with 5g of water swellable polyurethane polymer was hollowed in the center, and this was filled with the following formulation:

| | |
|----------|--------------------------------------|
| 20g | D.I. Water |
| 15 grams | Graphite Fiber |
| 5 grams | Water Swellable Polyurethane polymer |

Into the center was inserted a stainless steel rod.

In both instances, the extraction cells used 200 ml of a 0.01 molar solution of sodium chloride.

Observations:

At the end of 3 hours of cell operation, the stainless steel anode elements were removed from the test setup and examined. The control anode was observed to have decomposed completely, filling the HRM with corrosion products. The sample containing the inner layer of electrically conductive graphite filled polymer displayed no corrosion of the stainless steel rod.

It was apparent that the additional power demand of the control anode was caused by the corrosion of the metal.

WHAT IS CLAIMED IS:

1. A process for extracting ions from a bulk source comprising introducing a host receptor matrix into contact with the bulk source, inducing ion migration from the bulk source into the host receptor matrix by means of an external electropotential gradient, and removing said matrix from the bulk source, wherein said matrix provides a means for immobilizing said ions and facilitates the maintenance of a substantial electropotential over the desired ion removal period.
2. The process of claim 1, wherein said ions are cations.
3. The process of claim 1, wherein said ions are anions.
4. The process of claim 1, wherein said ions are radionuclides.
5. The process of claim 1, wherein said ions are heavy metals.
6. The process of claim 1, wherein said ions to be immobilized are rendered ionic by the use of surfactants or colloidal species.
7. The process of claim 1, wherein said host receptor matrix includes a polymeric material.
8. The process of claim 1, wherein said host receptor matrix includes a ceramic composite.
9. The process of claims 1, 7 and 8, further comprising the steps of withdrawing and transporting said host receptor matrix away from said bulk source.
10. The process of claim 9, further comprising the step of processing said host receptor matrix into disposable waste.
11. The process of claims 1 and 7, further comprising introducing an extractant reagent into the bulk source to enhance ion mobility.
12. The process of claim 11, wherein said extractant reagent is a fertilizer or soil nutrient.
13. The process of claim 12, wherein said extractant reagent is a fertilizer solution which includes an ammonium ion.

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14. The process of claims 1 and 7, wherein said process is conducted in-situ.
15. An apparatus for extracting ions from a bulk source comprising a pair of electrodes, means for creating an electropotential between said electrodes and an ion conducting polymeric host receptor matrix which is associated with at least one electrode, wherein said matrix is receptive to the ions to be extracted and said matrix and said electrodes are configured to facilitate maintenance of a substantial electropotential over the desired ion removal period.
16. The apparatus of claim 15, wherein said host receptor matrix is capable of interdicting ions which are caused by said electropotential to migrate from said bulk source toward said host receptor matrix.
17. The apparatus of claim 15, wherein said ion conducting polymeric host receptor matrix comprises a mass polymer which provides structural integrity and an ion conductive polymer having pendant ion exchange sites.
18. The apparatus of claim 17, wherein said host receptor matrix facilitates ion migration toward said electrodes while resisting counter-ion migration.
19. The apparatus of claims 17 and 18, wherein said mass and ion conductive polymers are intertwined.
20. The apparatus of claims 17 and 18, wherein at least one of said polymers is a hydrophilic organic polymer.
21. The apparatus of claims 15 and 16, wherein the anode of said pair of electrodes has associated therewith a polymeric host receptor matrix, said matrix comprising an electrically conductive polymer adjacent to the anode which is capable of protecting the anode from deterioration, thereby enhancing the operational life of said apparatus.
22. A host receptor matrix useful for electrochemically removing ionic materials from a bulk medium comprising a mass polymer which provides structural integrity and

- an ion conductive polymer having pendant ion exchange sites.
23. The host receptor matrix of claim 22 wherein at least one of said polymers is hydrophilic.
 24. The host receptor matrix of claim 22, wherein said matrix is associated with at least one of a pair of electrodes.
 25. The host receptor matrix of claim 24, wherein said matrix is capable of inducing ion migration toward said at least one electrode while resisting counter-ion migration.
 26. The host receptor matrix of claims 24 and 25, wherein said matrix comprises a multilayered composite, at least one layer being ion conductive and at least one layer being positioned adjacent the anode and functioning to enhance the electrolytic stability of the anode.
 27. The host receptor matrix of claim 26, wherein said at least one layer positioned adjacent the anode is an electrically conductive carbon filled polymer.
 28. The matrix of claims 22, 24 and 25, further comprising a component which immobilizes selected radionuclides or heavy metals by ion exchange or ion chelation.
 29. The matrix of claims 22, 24 and 25, further comprising a component which reacts with ions produced at the electrode to insolubilize or neutralize said ions.
 30. The matrix of claims 22 and 23, wherein at least one of said polymers is resistant to attack by hydroxyl or hydrogen ions.
 31. The matrix of claims 22, 24 and 25, wherein the mass polymer includes a ceramic material.
 32. The matrix of claim 31, wherein the mass polymer is an open cell glass foam.
 33. The matrix of claim 31, wherein the mass polymer is a porous alpha-alumina material.
 34. The matrix of claims 22, 24 and 25, further comprising a component which minimizes electrode polarization.

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35. An in-situ extraction process for removing ions from a bulk source comprising inducing ion migration through at least one ion permeable membrane by means of an external electropotential and collecting said ions in a confinement chamber.
36. The process of claim 35, further comprising disposing of said ions by transporting said confinement chamber to an appropriate processing or burial site.
37. The process of claim 35, wherein said bulk source is a subterranean aquifer.
38. The process of claim 35, wherein said bulk source is the interstitial water surrounding the particles in a soil strata.
39. The process of claim 35, wherein said confinement chamber comprises a polymeric host receptor matrix.
40. The process of claim 39, wherein said ion permeable membrane comprises an outer layer covering said host receptor matrix.
41. The process of claim 35, wherein said confinement chamber comprises a ceramic matrix including ion exchange media.
42. A process for removing ionic solutes from a bulk source comprising imposing an electropotential by means of a pair of electrodes, at least one of which is substantially enveloped by a hydrophilic host receptor matrix, and collecting the ionic solutes which are transported by the electropotential to the host receptor matrix.
43. The process of claim 42, further comprising recovering said ionic solutes by removing said matrix from the bulk source and subsequently reversing the charge on the electrodes to force the ionic species out of the matrix.
44. An apparatus for extraction of ionic species from a bulk source comprising two oppositely charged electrodes at least one of which includes a structurally stable host receptor matrix, said

apparatus having a configuration that can accommodate introduction and retrieval of said host receptor matrix from a region proximate to the bulk source, said host receptor matrix being capable of receiving and retaining said ionic species.

45. The apparatus of claim 44, wherein said host receptor matrix is ion permeable and is capable of transmitting ions from the bulk source to the matrix or to the electrode where said ions are collected.
46. The apparatus of claim 44, wherein at least one of said electrodes is coated with a metal oxide.
47. The apparatus of claim 46, wherein at least one of said electrodes is titanium coated with ruthenium oxide.
48. The apparatus of claims 44 and 45, wherein the apparatus is contained in a substantially cylindrical housing.
49. The apparatus of claims 44 and 45, wherein the host receptor matrix is introduced as a sheet membrane covering the region proximate to the bulk source.
50. The apparatus of claims 44 and 45, wherein at least one electrode is a sheet membrane comprising an electrically conductive polymer.
51. The apparatus of claims 44 and 45, in communication with the bulk source in a tank or storage vessel to remove ionic species from said bulk source.
52. The apparatus of claims 44 and 45, in communication with the bulk source in a pipeline to remove ionic species from said bulk source.
53. The apparatus of claims 44 and 45, wherein the host receptor matrix is an alpha alumina ceramic composite within a high pressure or hostile atmosphere, said matrix being configured such that a concentrated ion solution can be drawn away from the bulk source.

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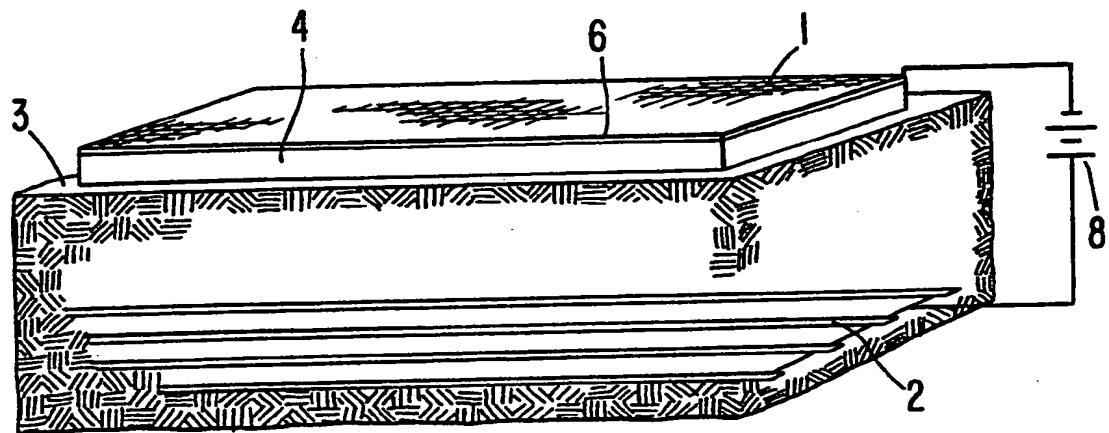
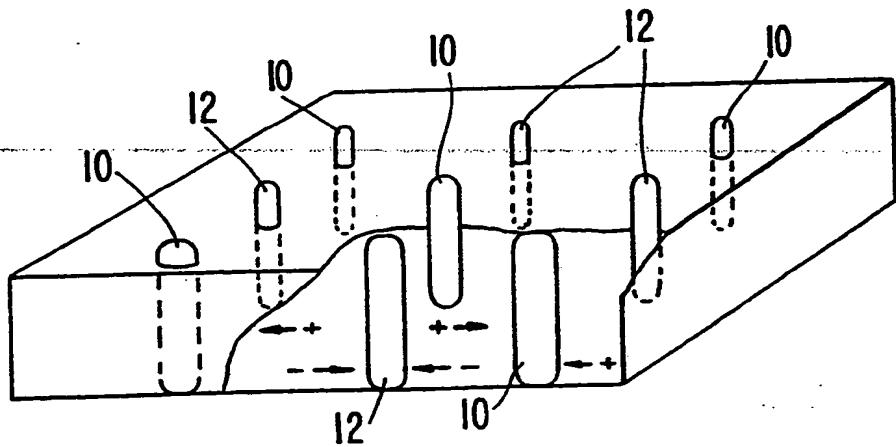
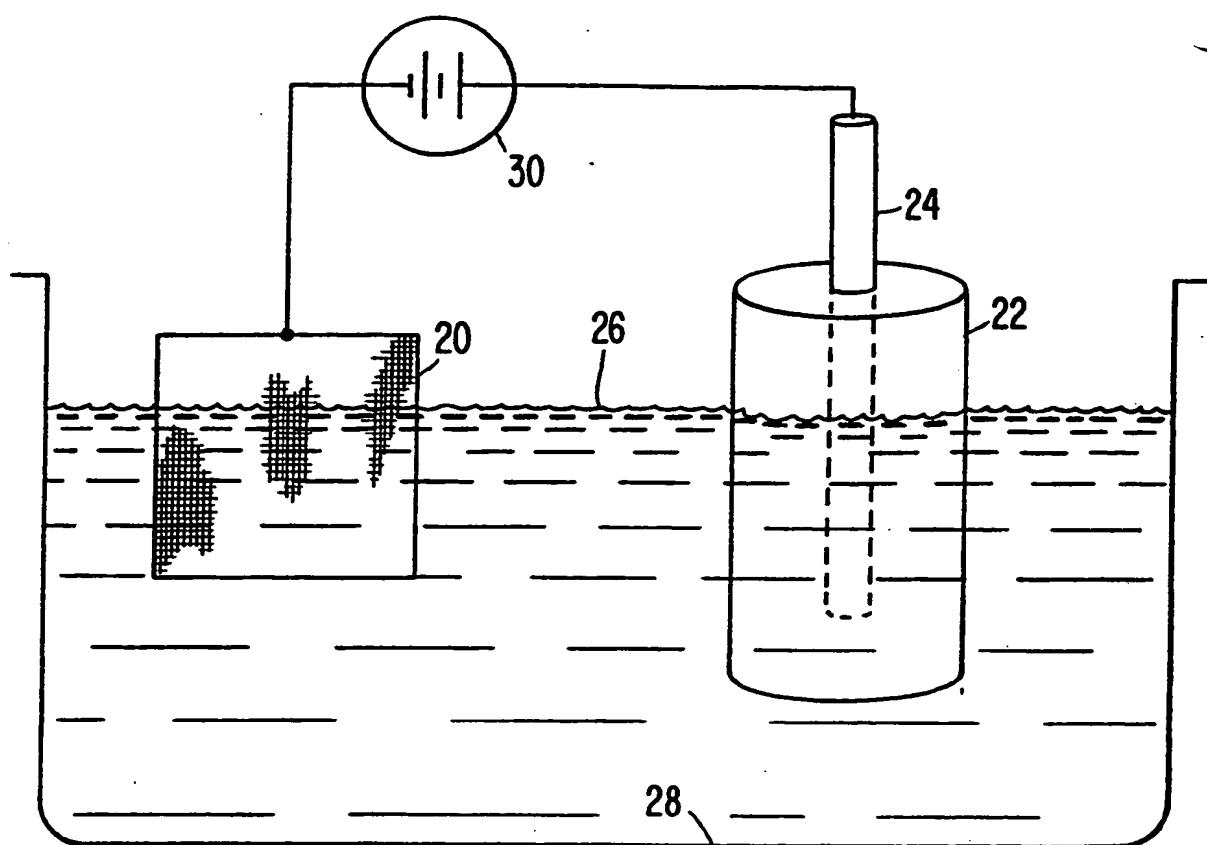
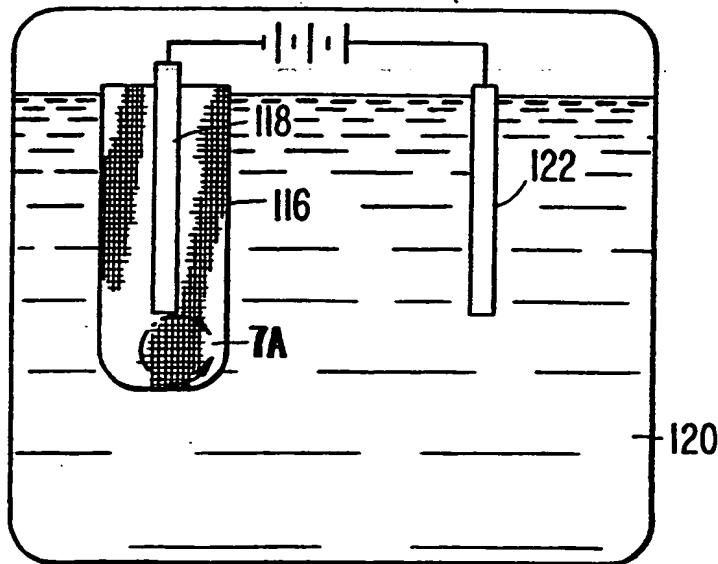
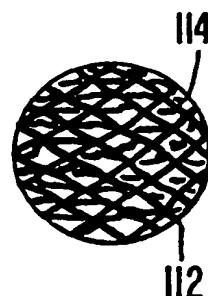
FIG. 1**FIG. 2.**

FIG. 3**FIG. 7****FIG. 7A****SUBSTITUTE SHEET**

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FIG. 4

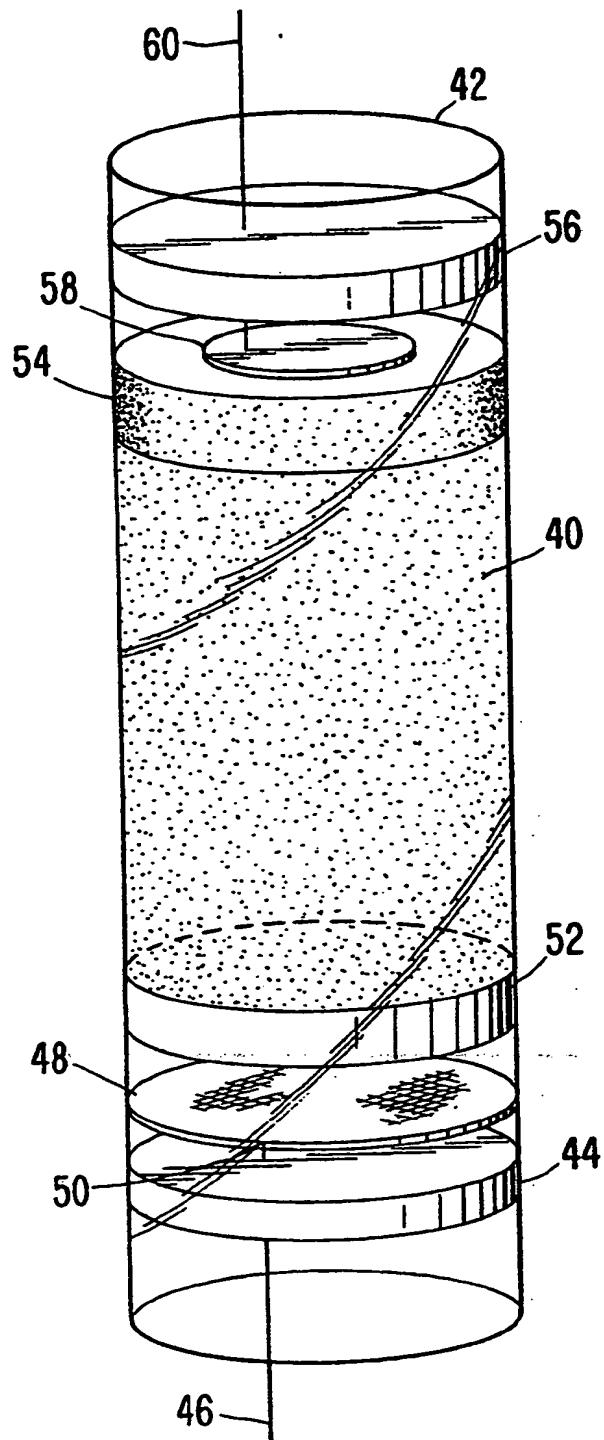
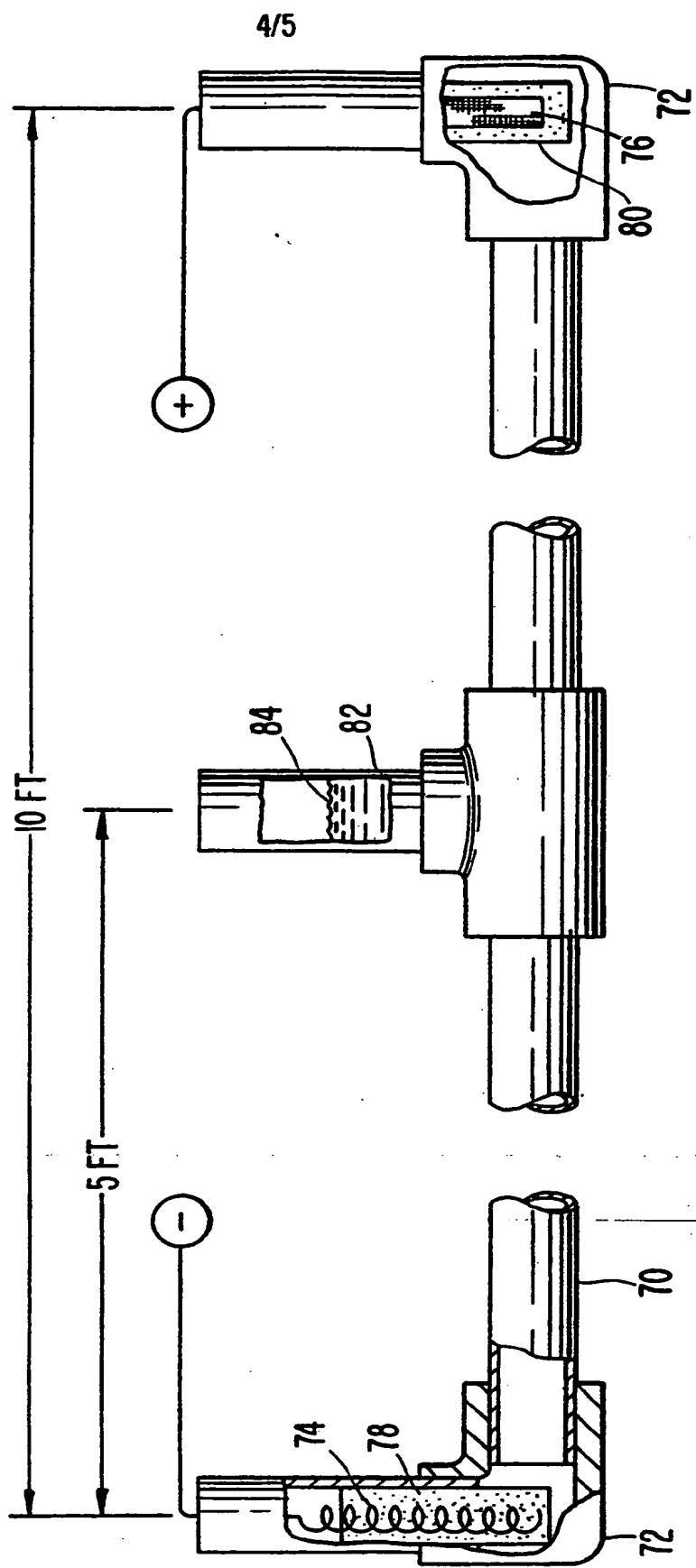
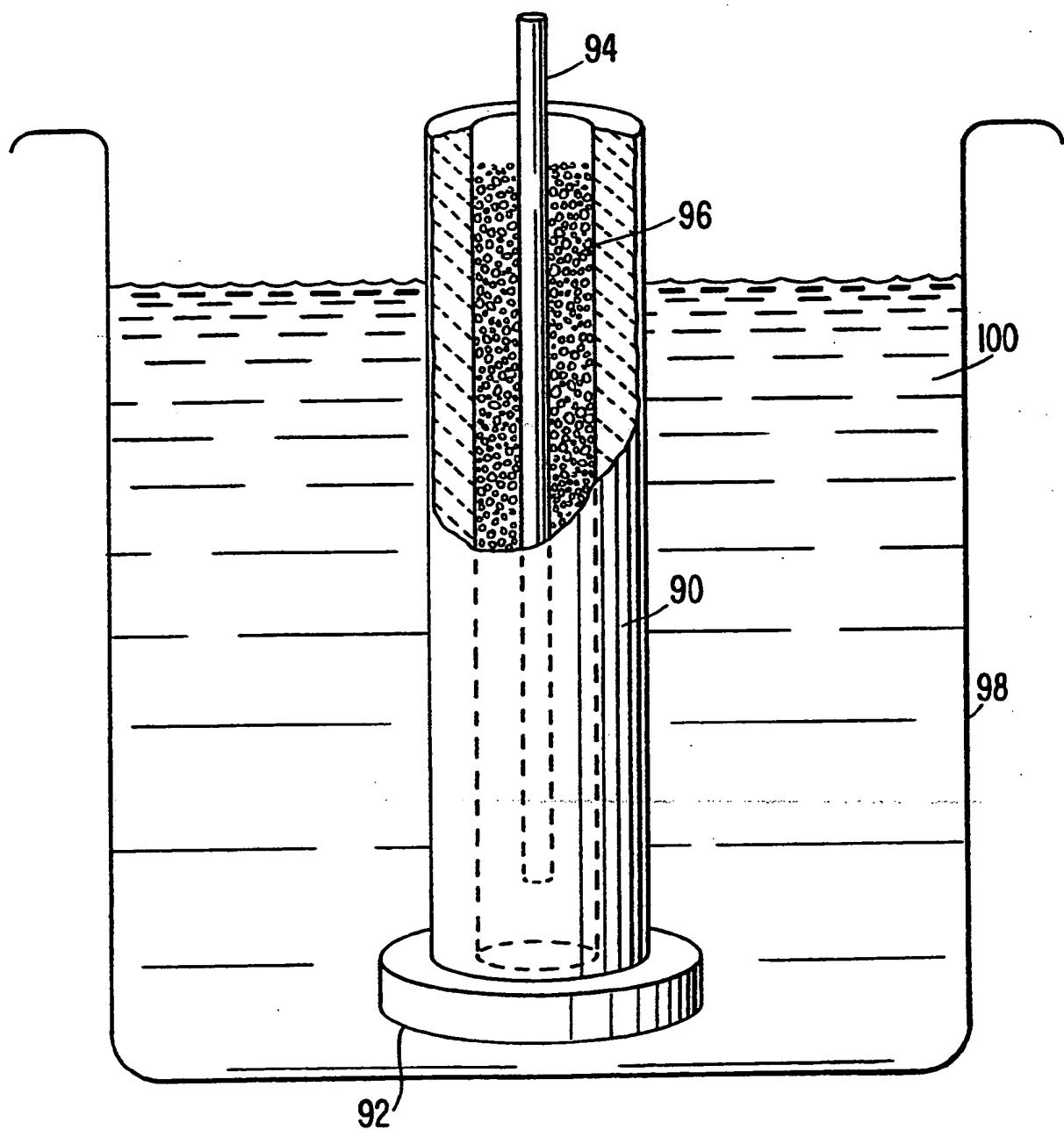


FIG. 5



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FIG. 6



SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US90/03997

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ¹⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(5): C25C 1/22, B09B 1/00

US CL.: 204/1.5, 405/128

II. FIELDS SEARCHED

Minimum Documentation Searched ¹⁷

| Classification System ¹⁸ | Classification Symbols |
|-------------------------------------|---------------------------------|
| US | 204/1.5 204/dig. 13, 405/128 |

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ¹⁹

III. DOCUMENTS CONSIDERED TO BE RELEVANT ²⁰

| Category ²¹ | Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷ | Relevant to Claim No. ¹⁷ |
|------------------------|--|-------------------------------------|
| A | US, A, 2,739,934 KUNIN, 27 MARCH 1956 | 1-8 |
| A | US, A, 2,832,728 KUNIN, 29 APRIL 1958 | 1-8 |
| A | US, A, 4,188,266 FORMAN, 12 FEBRUARY 1980 | 1-8 |
| A | US, A, 4,234,393 HEPWORTH ET AL. 18 NOVEMBER 1980 | 1-8 |
| X | US, A, 4,338,215 SHAFFER ET AL. 06 JULY 1982 | 1-8 |
| X | US, A, 4,632,847 LOMASNEY 30 DECEMBER 1986 | 1-8 |

* Special categories of cited documents: ¹⁵

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search ²²

19 OCTOBER 1990

International Searching Authority ²³

ISA/US

Date of Mailing of this International Search Report ²⁴

12 DEC 1990

Signature of Authorized Officer ²⁵

For Andre Relincon
NGOCLAN MAI

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET**V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹**

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. Claim numbers . because they relate to subject matter¹ not required to be searched by this Authority, namely:

2. Claim numbers . because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out¹, specifically:

3. Claim numbers 9-14, 19-21, 26-34, 48-53, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING²

This International Searching Authority found multiple inventions in this international application as follows:

- I. Claims 1-8, drawn to a process for extracting ions
- II. Claims 15-18, drawn to an apparatus for extracting ions
- III. Claims 22-25, drawn to a hose receptor matrix
- IV. Claims 35-41, drawn to an in-situ extraction process
- V. Claims 42-43, drawn to a process for removing ionic solutes

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

VI. Claims 44-47, drawn to an apparatus for extracting ionic solutes

3. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

1-8

4. As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.